

med. biochem

*Organophosphate - 1510 (F)*

Significance of phosphorus in formation of hydroxytetracycline.

Z.M.Zaitseva and N.V.Orlova (All Union Antibiotic Res.Inst.). Doklady Akad.Nauk SSSR, 124, 436-39 (1959).

It was shown by growth of cultures of Act. rimosus that added P in the medium energizes the synthesis of nucleic acids, especially in the II phase of micellar growth. Acid-insol. polyphosphates are absent as a rule, but a difficultly hydrolyzable form of P accumulates to extent of 0.8% in the mycellium. Metabolism in general is stimulated by excess P in the medium, with increased yield of volatile acids, AcOH and pyruvic acids especially. However, excess P tends to reduce the yield of hydroxytetracycline by 3-6 fold. Addn. of excess P shifts the time of maximum P content in the mycellium to the 24 hrs. rather than normal 16 hrs. of duration of culture growth. Cf. Guberniev et al., Antibiotiki, No.3, 8 (1956).

G.M.Kosolapoff.

Bio

Some data on the mechanism of synthesis and utilization of polyphosphates in yeast

B. Bukhotich and A.M. Belozerskii. (M.V. Lomonosov State Univ., Moscow). Doklady Akad. Nauk SSSR 124, 1147-49 (1959).

Yeast (baker) is capable of incorporating  $P^{32}$  in the presence of dinitrophenol, the incorporation being in the orthophosphate and acid-soluble stable phosphorus compounds; entry into all other P derivs. is blocked. Removal of dinitrophenol results in rapid decline of the stable acid-sol. form and a rise in labile acid-sol. P. Adenosinetriphosphate activity also rises rapidly at this stage along with acid-insol. polyphosphates. Evidently the acid-sol. stable P passes into a labile form which is not a polyphosphate nor adenosinetriphosphate. Yeast were also grown on radioactive (P) or non-radioactive medium for 3 hrs., after which they were placed in P-free medium. This transfer results in rapid rise of ATP activity to the level of polyphosphates, possibly owing to a direct transfer of polyphosphate P to the adenylic system, which then controls the various synthetic routes. The orthophosphate activity rises rapidly after the transfer also and reaches the polyphosphate activity level in 15 min. The possible paths of polyphosphate metabolism are shown on a suggested chart.

G.M. Kosolapoff.

W Precursors of purines of nucleic acids in higher plants.

G.I. Semenenko (A.M. Gorky State Univ., Kharkov). Doklady Akad. Nauk SSSR, 124, 1150-53 (1959). Bio

Wheat and corn plants were grown in nutrient media and examined for purine content. Purine content rises in sprouts <sup>with</sup> ~~removal of~~ the endosperm being intact. The best precursor for purines for sprouts with removed endosperm was glycine. Ribonucleic acid hydrolysate was also rather effective.  $C^{14}$ -labelled glycine (carboxyl label) shows active  $C^{14}$  incorporation into the purines. Wheat sprouts do not utilize nucleic acid purines for nucleic acid synthesis. The glycine incorporation involves adenine and guanine.

G.M. Kosolapoff.

**Pigment synthesis in the roots.**

Bio

B. A. Rubin and V. F. Germanova (M.V.Lomonosov State Univ., Moscow). Doklady Akad. Nauk SSSR, 124, 940-43 (1959).

It was shown that roots of bean, sunflower and nasturtium plants are capable of synthesizing green and yellow plant pigments in approximately the same proportions as are found in the plant leaves, when the roots of the exptl. plants are kept under illumination. Thus, the bean plants form more chlorophyll than sunflower plants, while nasturtium forms the least amount. Carotenoids are formed to the greatest degree in sunflower roots or leaves. The plants which show a high order of synthetic activity for the green pigments also show a high order of activity of catalase and cytochromeoxidase in the roots.

G.M.Kosolapoff.

Bio

**Effect of extraradical feeding on the alkaloid content and chlorophyll content in Datura inermis plants leaves.**

S. B. Shpil'nyaya (S.M.Kirov Milit.Med.Academy, Moscow). Doklady Akad. Nauk SSSR, 124, 944-46(1959).

Spraying of the above plants with solns. of  $(\text{NH}_4)_2\text{SO}_4$  (1-2%) for extraradical feeding, resulted in improved growth of the plant and increased its alkaloid yield by some 50% at ripening period of the fruit.

G.M.Kosolapoff.

Bio

Effect of X-radiation on the content of nitrogenous substances in wheat.

I. M. Vasil'ev, O. I. Parfenova and N. D. Pybalka. Doklady Akad. Nauk SSSR, 124, 928-29 (1959).

It was shown that 5000 r dose of X-radiation which totally suppressed the growth of 5-6 day wheat sprouts (winter wheat) does not suppress the formation of nucleotides and cyclic amino acids in the plants which form readily under conditions which are normally favorable for photosynthesis over several day period following the irradiation. The detection of the products was done spectrophotometrically only.

G.M.Kosolapoff.

Effect of chronic  $\gamma$ -irradiation on mouse blood.

Bio

E. N. Kopylova. Doklady Akad. Nauk SSSR, 124, 930-32 (1959).

Mice subjected to daily dose of  $\text{Co}^{60}$   $\gamma$ -radiation at 0.05-0.4 r daily show the symptoms of leuco- and lymphopenia after approximately a year. A daily dose of 0.1r produces hyperregeneration of white blood cells over that period. The small daily doses of radiation eventually cause a reaction which suppresses leucopoiesis.

G.M.Kosolapoff.

Bio

Spectrophotometric study of the effect of pH and ionic strength on the stability of high polymeric ribonucleic acid in solution.

L. P. Gavrilova, A.S.Spirin and A.N.Belozerskii (A. N. Bakh Biochem. Inst., Moscow). Doklady Akad. Nauk SSSR, 124, 933-36 (1959).

It was shown that below pH 5 and above pH there exist zones of instability of highly polymeric ribopolynucleotide, possibly at the internucleotide link to the ester groups. Between these limits, the substance is stable in any ionic strength of acetate, phosphate or glycine buffer soln.

Cf. Reddi et al. Nature, 180, 374 (1957).

G.M.Kosolapoff.

**Experimental formation of active variants of Aspergillus niger which form citric acid.**

A. A. Imshenetskii, L. I. Solntseva and N. F. Kuranova. Doklady Akad. Nauk SSSR, 124, 925-27 (1959).

The commercial strain of A. niger subjected to ultraviolet light is prone to yield a mutant form, which forms colonies of different shape, which has a smaller dry weight of the mycelium, consumes more sugar and produces more citric acid than the original strain ( yield may be as high as 74% ). Gluconic and oxalic acid are formed in negligible amounts by the mutant.

G.M.Kosolapoff.

bio

Structure of erysimoside -- a steroidal diglucoside from plants of *Erysimum* species.

V. A. Maslennikova, F. S. Khristulas and N. K. Abubakirov (Plant Substances Chem. Inst., Uzbek. Acad. Sci. ). Doklady Akad. Nauk SSSR, 124, 822-25 (1959). Paper chromatography with 1:1:1 MePh, BuOH and  $H_2O$  solvent system resulted in isolation from the *Erysimum* glucosides of a new substance named erysimoside,  $C_{35}H_{52}O_{14}$ , (I), amorphous solid,  $[\alpha]_D^{30} 16.5^\circ$ , which gives the color tests typical of cardiac glucoside of the digitalis group; prolonged action of  $Ac_2O$ -pyridine gave an acetyl deriv., dec.  $221-23^\circ$ ,  $[\alpha]_D^{25} 33.9^\circ$ , which appears to be a pentaacetate, which saponifies to I with  $MeOH-KHCO_3$ . Hydrolysis with pancreatic juice of *Helix plectotropis* cleaves I to hexose and a monoglucoside; the hexose is D-glucose. The residual desglucoerysimoside forms needles,  $C_{29}H_{42}O_9$  (from 60% MeOH), without a constant m.pt. Prolonged drying over  $P_2O_5$  gave a product, m.  $174-75^\circ$ ,  $[\alpha]_D^{20} 32.4^\circ$ ; vacuum drying gave a specimen, m. ~~152-55~~<sup>152-55</sup> $^\circ$ . This gave color tests typical of a cardiac glucoside with a 5-membered lactone ring; the positive Keller-Kiliani test indicates that the aglucone is linked to a 2-desoxy sugar. In the above ternary solvent system this moves with strophanthidine (Rf 0.85), but 1:1  $CHCl_3$ -MePh separates these 2 substances. With  $Ac_2O$ -pyridine it gave a diacetyl deriv., m.  $242-43^\circ$ ,  $[\alpha]_D^{20} 35.5^\circ$ ; no carbonyl group derivs. could be prep'd. Mild acid hydrolysis of desglucoerysimoside gave an aglucone, prisms, m.  $176-77^\circ$ ,  $[\alpha]_D^{19} 48.6^\circ$  (monoacetyl deriv., m.  $243^\circ$ ; phenylhydrazone, m.  $241-42^\circ$ ), identified as strophanthidine. The sugar component of the hydrolysis mixture was D-digitoxose. The results indicate that erysimoside is strophanthidine (3)-D-digitoxosido-D-glucoside. It and olitoriside are diastereoisomeric substances. If the plant seeds are allowed to ferment for 3 days prior to isolation of the glucosides, the main isolable product of the glucoside group was desglucoerysimoside. The latter appears to be identical with helveticoside (Nagata et al. Helv. Chim. Acta, 40, 41 (1957)) and erysimotoxin (Maksyutina, Zhur.Obsh.Khim. 28, 1383 (1958)).

G.M. Kosolapoff.

Bio

An organospecific liver antigen which is absent in hepatoma.

G.I. Abslev, Z.A. Avenirova, N.V. Engel'gardt, Z.L. Baidakova and G.I. Stepanchenok-Rudnik. Doklady Akad. Nauk SSSR, 124, 1328-30 (1959).

Examn. of cytoplasmic liver granules of mice with transplanted mouse hepatoma ~~Expt~~ (cf. Zil'ber et al. this j. 124, No. 4 no pp (1959)) showed that in hepatoma the mouse liver lacks an antigen factor (named AO), which under normal conditions shows a very specific precipitation reaction and is found only in the liver. For isolation of this from normal mice an ultrasonic irradiation in veronal-medial buffer was used, since this antigen is more strongly bound to the cell walls than are other antigens. This reacted only with anti-MmP sera and did not react with antihepatomic sera. (MmP-mitochondrial and microsomal fraction of normal liver). AO did not migrate in electrophoresis but this showed the presence in AO of a ballast lipoprotein. It is suggested that AO is principally a polysaccharide.

G.M. Kosolapoff.

Bio

Oxidative phosphorylation in the liver under the action of high oxygen pressure and introduction of I-131.

Z.G. Bronovitskaya (State Univ., Rostov-on-Don). Doklady Akad. Nauk SSSR, 124, 1331-34 (1959).

The phosphorylation coeff. was studied in rat livers under 6 atm.  $O_2$  pressure ~~in the presence of I-131~~. The expts. were run until violent convulsions of the animals produced a severe state of well-being. The results indicate that prolonged existence under high  $O$  pressure dissociates respiration from phosphorylation in the liver. High-energy compds. tend to accumulate in the liver and ATP content tends to drop owing to its consumption in the formation of these substances, as shown by lowered synthesis of ATP. Similar expts. with rabbits treated with  $I^{131}$  showed decreased assimilation of  $O$  and increased binding of inorg. P, with increased liver phosphorylation function.

G.M. Kosolapoff.

Nucleotide composition of nucleic acids of *Bombyx mori*. Bio

N.M.Sisakyan and N.A.Gumilevskaya (A.N.Bakh Biochem. Inst., Moscow). Doklady Akad. Nauk SSSR, 124<sup>4</sup>, 1154-56 (1959).

The content of guanylic, adenylic, cytidilic and uridilic acids in pupae of *Bombyx mori* is tabulated. The results agree with the regularities observed by Chargaff (Biochem. Biophys. Acta, 17, 367 (1955)). Deoxyribonucleic acid content in this organism is rather low but the individual distribution again agrees with Chargaff's regularities (Experientia, 6, 201 (1950)).

G.M.Kosolapoff.

Selective inhibition of activity of oxidation-reduction enzymes in tumor cells after action of chain reaction inhibitors. Bio

N.M.Emanuel, L.P.Epichina, I.I.Pelevina and T.E.Lipatova. Doklady Akad. Nauk SSSR, 124, 1157-59 (1959).

The following expts. were run in vitro with tumor tissues from mice (various types of cancerous growths) and rabbits. Propyl gallate acts selectively on tumor cells at 0.75% concn. This action consists of repression of dehydrogenase activity and cytochromoxidase activity. The treated cells cannot be transplanted any longer and retain their activity as tumor cells.

G.M.Kosolapoff.

Peculiarities of electron structure of nucleic acids and their protein complexes. Bio

L.A.Blyumenfel'd, A.E.Kalmanson and Shen Pei Gen. Doklady Akad. Nauk SSSR, 124, 1144-46 (1959).

Electron paramagnetic resonance spectra of nucleic acids and their protein complexes are shown and discussed. While yeast ribonucleic acid shows no wide band in the spectrum, its complex with serum and egg albumin show a very wide and intense band with  $10^{21}$  unpaired electrons per g. The material remaining in soln. does not produce a spectrum. The no. of paramagnetic particles is constant in ~~20-100°~~ temp.range down to 100°K, then drops to zero

G.M.Kosolapoff.



Reparative processes in the skin of young dogs after introduction of cortisone and the adrenal cortical hormone principle.

BiO

A.I.Bukhonova. Doklady Akad. Nauk SSSR, 124, 477-80 (1959) (Voronezh State Med. Inst.).

Expts. with young pups from which a skin section had been removed while cortisone administration was being made daily at 20 mg daily (same for the adrenal hormone ext.) showed the course of the regenerative process, which is illustrated by numerous photographs. Both substances disrupt the formation of granulation tissues but accelerate its growth; the tissue tends to form superabundant amounts of dense connective tissue with high collagen content. The process of premature development and aging of the skin is observed.

G.M.Kosolapoff.

BiO

Effect of streptomycin on green coloration of sprouts.

B.A.Rubin and M.E.Ladygina (A.N.Bakh Biochem.Inst., Moscow). Doklady Akad. Nauk SSSR, 124, 1163-66 (1959).

Streptomycin inhibits the cytochromoxidase activity in barley sprouts, the effect being blocked by Fe or  $Mn^{++}$ . These effects are directly correlatable with alterations in synthesis of chlorophyll by the plants. Thus, streptomycin by its effect of cytochromoxidase tends to retard chlorophyll formation and the green coloration of the sprouts. Fluorescence photography of sprouts of barley showed that the fluorescence spectra of plants with or without streptomycin are similar provided that light were excluded from the growing sprouts. The albino plants produced by streptomycin show spectra indicative of transition stages between protochlorophyll and chlorophyll. Evidently streptomycin tends to retard this transformation specifically.

G.M.Kosolapoff.

**Action of intensity and spectral composition of radiation on metabolism and crop.**

*Bio*  
N.F.Voskresenskaya and G.S.Grishina (K.A.Timiryazev Plant Physiol.Inst., Moscow). Doklady Akad. Nauk SSSR, 124, 469-72 (1959).

Expts. with kidney bean plants with environment being varied by the use of various levels of illumination with either red or blue lamps, showed that blue light aids the protein accumulation in the leaves, the effect being more pronounced at light light intensities. The cytochrome system activity is higher in leaves grown in blue light, as an adaptation phenomenon evidently. Protein synthesis is aided by the blue light, this effect leading to a rise in seed crop and that of accumulated nitrogenous products.

G.M.Kosolapoff.

*Bio*  
**Volatile emanations of flowers and alteration of sex symptoms in corn.**

G.V.Porutskii and S.V.Cherednichenko. Doklady Akad. Nauk SSSR, 124, 473-76 (1959).

The connection between activity of volatile products and sex symptoms changes in corn was examined by introduction of radioactive thiamine into the plants during flowering, with subsequent tracing of later generations. The results indicate that radioactive thiamine aids the predominant development of the stamen- carrying flowers with a sharp reduction of the activity of the volatile excretions of the individual flowers; the activity of the volatiles from pistillate flowers rises at the same time. Typical plants are shown. Irregular ears of corn are commonly produced.

G.M.Kosolapoff.

Some data on invertase activity in isolated lucerne roots.

Bio

M.S.Bardinskaya, A.M.Smirnov and V.I.Safonov (K.A.Timiryazev Plant Physiol. Inst., Moscow). Doklady Akad. Nauk SSSR, 124, 462-65 (1959).

The isolated lucerne roots from plants grown for prolonged periods in sterile medium possess noticeable amounts of invertase which can cleave sucrose and which can accomplish the transfer reactions forming oligosaccharide containing fructose and -methylfructoside. The activity of the enzyme drops by 7 days of culturing and at this time the nutrient medium begins to show a rise in alkalinity. The enzyme concn. is highest in the growth zones of the roots.

G.M.Kosolapoff.

Bio

Effect of environmental conditions on respiration intensity in cuttings treated with heteroauxin.

V.F.Verzilov and L.V.Runkova. Doklady Akad. Nauk SSSR, 124, 466-8 (1959).

Expts. with bean plant cuttings which were rooted at 12-14° or 18-20° under various light intensities and with or without treatment with heteroauxin, showed that the treatment lowers the respiration level in cuttings kept at 18-20° with strong illumination in the leaf tissue but raises it in the lower parts of the stem, this being true during root formation. The heteroauxin action was lower at lower temp. and lower light intensity. Thus the heteroauxin effect is aided by higher temp. and more intense light.

G.M.Kosolapoff.

Bio

**Influence of penicillamine on decarboxylation of amino acids by microbial preparations.**

S.R.Mardashev and L.A.Semina (I.M.Sechenov 1st Moscow Med. Inst.). Doklady Akad.Nauk SSSR, 124, 456-58 (1959).

Penicillamine added at  $10^{-2}$ - $10^{-4}$ M concns. to cultures of *Bac. cadaveris* blocks the decarboxylation of lysine, the effect being rather weak at  $10^{-4}$ M, but pronounced at  $10^{-2}$ M. *E. coli* decarboxylase is similarly repressed in its decarboxylation of arginine substrate by the presence of penicillamine. Other microbial specimens gave results that were not clear-cut. Al, Fe, Cu or Zn ions do not remove this blocking effect of penicillamine. Cf. Snell et al. JACS 76, 4745 (1954). G.M.Kosolapoff.

Bio

**Participation of alanine in biosynthetic processes in plants.**

E.A.Shilov and A.A.Yasnikov (Inst. Org. Chem., Kiev ). Doklady Akad. Nauk SSSR, 124, 459-61 (1959).

The participation of alanine in biosynthetic processes in plants (kok-sagyz) evidently depends on the ability of alanine to form  $\text{AcOH}$  and  $\text{MeC}(:\text{NH})\text{H}$  as precursors for other products.  $\text{C}^{14}$ -labelled alanine specimens were traced through the kok-sagyz plants showing: very rapid  $\text{C}^{14}$  uptake from alanine into the rubber, cellulosic matter, fatty acids but very little in glycerol. The incorporation of  $\text{C}^{14}$  from alanine in carotene is relatively slow. The possible reaction courses are discussed.

G.M.Kosolapoff.

Bio

The paths of influence of ionizing radiation on the content of free nucleotides and nucleosides in bone marrow cells.

V.Ya.Brodskii, E.Ya.Graevskii and I.A.Suetina (A.N.Severtsov Animal Morphol. Inst., Moscow). Doklady Akad.Nauk SSSR, 124, 440-43 (1959).

X-irradiation ( 700 r ) of white mice at 94 r/min. results in decline of the nucleotide content in the animal tissue, whether directly irradiated or screened from direct radiation. The results were shown graphically.

Cf. Brodskii et al. Biofizika, 3, 92(1958). G.M.Kosolapoff.

Bio

Electrophoretic properties of some protein components of blood clotting.

B.A.Kudryashov, G.V.Andreenko and G.V.Kukushkina. (M.V.Lomonosov State Univ., Moscow). Doklady Akad. Nauk SSSR, 124, 452-55 (1958)

Electrophoretic sepn. of X and VII blood clotting factors isolated from sera of horse and rat blood was studied and the electrophorograms are shown. Factor VII is inhomogeneous and shows 2 bands indicative of  $\alpha$ - and  $\gamma$ -globulins with the <sup>former</sup> ~~latter~~ predominant. Factor X is practically completely composed of  $\gamma$ -globulins. Almost 100% of factor X protein and 81% of factor VII protein is collected in the electrophoretic peaks. The results indicate that factors VII and X and thrombotropin all have different electrophoretic mobilities. Thrombotropin is homogeneous and is composed of  $\alpha$ -globulin. It is possible that factor VII is blood thrombokinase and thrombotropin, these being the immobile and the mobile fractions, respectively, in electrophoresis.

G.M.Kosolapoff.

*O. N. N. N.*  
Nitrogen bond equivalence in tetramethylammonium bromide.

A. T. Babayan, M. G. Indzhikyan and M. B. Neiman. Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 174.

$C^{14}H_3Me_3NBr$  was prepd. from  $(C^{14}H_3)_2SO_4$  by treatment with  $KBr$  and  $Me_3N$ , the last reaction being run at  $-80^\circ$ . The resulting product was treated with  $K$  in  $NH_3$  over 1 week; the resulting  $CH_4$  was analyzed for  $C^{14}$  content. The resulting  $Me_3N$  was converted to  $HCl$  salt and burned for  $C^{14}$  analysis. It was shown that the evolved  $CH_4$  carried 23% of  $C^{14}$ , while  $Me_3N$  contained 78%. Thus the work confirms the equivalent nature of  $N$  bonds in  $Me_4NBr$ .

G.M. Kosolapoff.

*Organic*

A synthesis of 1,1-dicyclopentylethane and 1,2-dicyclopentylpropane based on cyclopentadiene.

V. I. Stanko and A. F. Plate (N. D. Zelinskii Inst. Org. Chem., Moscow).  
Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 115-120.

To 40 g. Mg under  $\text{Et}_2\text{O}$  there was added a mixture of 75 g.  $\text{EtOAc}$  and 174 g. 2-cyclopentenyl chloride in  $\text{Et}_2\text{O}$ ; after refluxing for 3 hrs. on the following day, the mixture was treated with dil.  $\text{H}_2\text{SO}_4$  yielding 58 g. bis-(2-cyclopentenyl), <sup>(I)</sup>  $b_{14}$  65.6°,  $n_D^{20}$  1.4941,  $d_{20}$  0.9072, and 22 g. bis-(2-cyclopentenyl)-~~methoxymethyl~~carbinol,  $b_8$  113-22°; repeated fractionation finally gave but 6 g. of the pure carbinol,  $b_{3-3.5}$  104.5-105.9°, 1.5121, 1.0014. Hydrogenation of I over Raney Ni in the cold in EtOH gave dicyclopentyl,  $b_{750}$  189.5-89.7°, 1.4650, -. Part of this was purified by passage over  $\text{SiO}_2$ , the other was frozen out; the pure product had f.p. -35.5° to -35.6°,  $n_D^{20}$  1.4643,  $d_{20}$  0.8656,  $b_{750}$  189.5-189.7°. ~~Reaction of AcCl with cyclopentene gave~~ Reaction of  $\text{AcCl}$  with cyclopentene gave methyl cyclopentyl ketone,  $b_{749}$  157.5-58°, 1.4432, 0.9161. This condensed with cyclopentadiene in the presence of  $\text{EtONa-EtOH}$  in 2 hrs. gave a crude product which was directly hydrogenated over Raney Ni at 90° to 9% 1,1-dicyclopentylethane,  $b_9$  98-100°, 1.4740, 0.8780. Alternatively, hydrogenation of methyl cyclopentyl ketone over Raney Ni at 90 atm. and 150° gave 1-cyclopentylethanol,  $b_{10}$  160-62°, ~~1.4570, 0.9189~~ 1.4570, 0.9189, which with  $\text{HBr-H}_2\text{SO}_4$  at 0°, room temp. and finally at steam bath temp 2 hrs. gave 1-bromo-1-cyclopentylethane, 39%,  $b_{7.5}$  49-50°, 1.4878, 1.2628, which was converted to the Grignard reagent and treated with 2-cyclopentenyl chloride, yielding a small amount of 1(2-cyclopentenyl)-1-cyclopentylethane,  $b_8$  96.5-97°, 1.4855, 0.8988, which hydrogenated over Raney Ni to 1,1-dicyclopentylethane, 21%,  $b_{14}$  102-102.5°, 1.47387, 0.8792. Reaction of cyclopentylmagnesium bromide with allyl chloride gave 57% allylcyclopentane,  $b_{749}$  125.8-26.2°, 1.4408, -, which with  $\text{HBr}$  at -30° gave 61% 2-bromo-1-cyclopentylpropane,  $b_{30}$  99.5°, 1.4818, 1.2126, which converted to the Grignard reagent and treated with 2-cyclopentyl chloride with ice cooling gave in 2 hrs. 55.5% 1-(2-cyclopentenyl)-2-cyclopentylpropane,  $b_{18}$  122.5°, 1.4796, 0.8832, which hydrogenated over Raney Ni

to 50% 1,2-dicyclopentylpropane,  $b_{14}$  117.5-18°, 1.47041, 0.8695, purified by passage over  $AlO_2$  and careful fractionation.

G.M. Kosolapoff.

*Organic* ~~*Al*~~ ~~*Organophosphorus*~~ (90)

Action of Raney nickel on ketones and acetals of the thiophene series.

Ya. L. Gel'dfarb and P. A. Konstantinov (N. D. Zelinskii Inst. Org. Chem., Moscow). Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 121-29. Cf. this j. 1956, 992.

Stirring 11 g. t-butyl 2-thienyl ketone and 80 g. Raney Ni in EtOH- $C_6H_6$  18 hrs. gave 41%  $Me_3CCOBu$ , b. 164-66°,  $n_D^{20}$  1.4163,  $d_{20}$  0.8211, whose 2,4-dinitrophenylhydrazone, m. 117.5-18°. Condensation of 3.36 g. 2,5-dimethylthiophene with 5 g. 2,5-dimethyl-3-thiophenecarboxylic chloride in  $C_6H_6$  in the presence of 7.5 g.  $SnCl_4$  gave 91% 2,2',5,5'-tetramethyl-3,3'-dithienyl ketone, m. 63-64° (from aq. EtOH). Reaction of  $SOCl_2$  with 2,5-bis-tert-butyl-3-thiophenecarboxylic acid gave the acyl chloride, 90%,  $b_7$  129-30° which with 2,5-bis-tert-butylthiophene in the presence of  $SnCl_4$  at 0°, finally at room temp., gave 80% 2,2',5,5'-tetra-tert-butyl-3,3'-diethienyl ketone, m. 213-18° (crude), m. 221-22° (from EtOH). Refluxing this with Raney Ni in EtOH- $C_6H_6$  gave no evidence of reaction even in 18 hrs. Stirring 25.4 g.  $POCl_3$ , 21.2 g  $PhNMeCHO$  0.5 hr. at room temp., addn. of 24 g. 2,2-di-(2-thienyl)-butane and keeping the mass overnight gave after an aq. treatment 64% 2-(2-thienyl)-2-(5-formyl-2-thienyl)butane,  $b_3$  160-62°, 1.6120, 1.2016; oxime, m. 103-104°. Refluxing 10.8 g. 2-thiophenecarboxaldehyde, 10 g.  $(CH_2OH)_2$  and 0.2 g. p-Me- $C_6H_4SO_3H$  in  $C_6H_6$  with continuous removal of  $H_2O$  over 16 hrs. gave 81% 2-thiophenecarboxaldehyde ethylene acetal,  $b_{24}$  121-22°,  $b_{15}$  110-11°, 1.5433, 1.2395. Similarly was prepd. 5-(2-thienyl)-2-thiophenecarboxaldehyde ethylene acetal,  $b_5$  178-81°,  $b_5$  179-80°, 1.5992, 1.2789; 5-butyl-2-thiophenecarboxald-



ehyde ethylene acetal, 77%,  $b_8$  132-33°, 1.5190, 1.0937; 2-(2-thienyl)-2-(5-formyl-2-thienyl)butane ethylene acetal,  $b_4$  187-88.5°, 1.5827, 1.2094. Treatment of 2-thiophenecarboxaldehyde ethylene acetal with Raney Ni in  $\text{Et}_2\text{O}$  12 hrs. gave 42% valeraldehyde ethylene acetal,  $b_{34}$  53-55°, 1.4211, 0.9269. Similarly 5-butyl-2-thiophenecarboxaldehyde ethylene acetal gave 53% pelargonaldehyde ethylene acetal,  $b_{17}$  113.5-15.5°, 1.4400, 0.9002, which on hydrolysis gave 2,4-dinitrophenylhydrazone, m. 106-107°, which agreed with an authentic specimen from pelargonaldehyde (cf. Strain, JACS 57, 758(1935)) 5-(2-thienyl)-2-thiophenecarboxaldehyde gave 33% capraldehyde ethylene acetal,  $b_{15}$  121-24°, 1.4390, 0.8923. 2-(2-thienyl)-2-(5-formyl-2-thienyl)-butane ethylene acetal gave 43%  $\delta$ -methyl- $\delta$ -ethylcapraldehyde ethylene acetal,  $b_7$  128-32°, 1.4530, 0.9024; the hydrolyzed specimen gave the 2,4-dinitrophenylhydrazone of the free aldehyde, m. 64.5-65.5°.

G.M.Kosolapoff,

*Organic*

Micro determination of the carbonyl group by oximation method.

V. A. Klimova and K. S. Zabrodina (N. D. Zelinskii Inst. Org. Chem., Moscow). Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 175-76.

The following micro detn. of CO groups is described; it is accurate within 0.2%. To 5 ml. of reagent soln. ( 0.7 g.  $\text{HONH}_2 \cdot \text{HCl}$ , 10 ml.  $\text{H}_2\text{O}$ , 0.5 g.  $(\text{HOCH}_2\text{CH}_2)_3\text{N}$  and 96% EtOH to give 100 ml.) was added 5-10 mg. of sample and the whole is kept 0.5 hr. at room temp. along with a blank. Then 2 ml. satd. NaCl soln. was added and 3 drops of indicator soln. (0.1 g. bromophenol blue in 100 ml. 20% EtOH ) and the soln. is titrated with 0.02N HCl to bluish-green color. To get a better color match with the blank. the test sample soln. is dild. with  $\text{H}_2\text{O}$  whose volume is about equal to the vol. of standard HCl indicating the difference between the 2 titrations and the content of CO is calcd. with due allowance for this diln. A variety of carbonyl compounds were successfully analyzed in this manner (table shown).

G.M.Kosolapoff.

3

Benzophenone and  $\text{Hg}(\text{OAc})_2$  in  $\text{C}_6\text{H}_6$  at  $70^\circ$  gave 92% oily diphenylacetoxy-acetoxy ~~chloromercurimethane~~, which gradually decomposed to  $\text{Ph}_2\text{CO}$  and  $\text{Hg}$ ; with alc.  $\text{CaCl}_2$  it gave diphenylacetoxychloromercurimethane, a solid which is rapidly decomposed on standing or on treatment with alkalis; with alc.  $\text{KOH}$  it gave  $\text{Ph}_2\text{CO}$  and  $\text{Hg}$ ; on heating to  $100^\circ$  it gave  $\text{Hg}$  and  $\text{Ph CO}$ . Similar reaction of  $\text{H}_2(\text{OAc})_2$  in  $\text{C}_6\text{H}_6$  with  $\text{o-O NC}_2\text{H}_2\text{CHO}$  hydrazones gave 80% oily, unstable o-nitrophenylacetoxycetoxymercurimethane, which with alc.  $\text{CaCl}_2$  gave a yellowish solid o-nitrophenylacetoxychloromercurimethane, dec. above  $135^\circ$  (from aq.  $\text{EtOH}$ ); with alc.  $\text{KOH}$  it gave  $\text{Hg}$  and the original aldehyde.

G.M. Kosolapoff.

*Organic*

An error.

E. Nikitina. Zhur. Obshchei Khim. 29, 696 (1959).

NO

Q

The paper in this j. 26, 621(1956) contains an error. At 109° the acid described therein should be a hydrate  $H_7[P(W_{27}O_7)_6] \cdot 4H_2O$ , not  $\cdot H_2O$ .

G.M. Kosolapoff.

~~Organophosphorus~~ (2)  
Extraction of ruthenium nitrosenitrate by extn. *Butyl phosphorus compounds*

A. V. Nikolaev and N. M. Spitsyn (Inorg. Chem. Inst., Siberian Section, Acad. Sci). Doklady Akad. Nauk S.S.S.R. 127, 117-9(1959).

Extn. of Ru nitrosenitrate from N HNO<sub>3</sub> was performed with (BuO)<sub>3</sub>PO, BuP(O)(OBu)<sub>2</sub> and Bu<sub>2</sub>P(O)OBu. The efficiency of extn. increased considerably in the above order of extractants, the last substance being able to effect a 88% extn. At very low concn.s of the extractants in the org. phase, the results were relatively close to each other. It is suggested that Me<sub>3</sub>C groups should give the highest extn. efficiency. Cf. Burger, J. Phys. Chem. 5, 62, 520 (1958).

G.M. Kosolapoff.

~~Original Source~~

**Extraction of nitric acid by derivatives of butylphosphonic acids.**

A. V. Nikolaev, S. M. Shubina and N. M. Sinitsyn (N. S. Kurnakov Inst. Gen. Inorg. Chem.). Doklady Akad. Nauk S.S.S.R. 127, 578-80 (1959). cf. Berger, J. Phys. Chem. 62, 590 (1958).

It was shown that  $\text{HNO}_3$  is extd. from aq. solns. progressively better by hydrocarbon solns. of  $(\text{BuO})_3\text{PO}$ ,  $\text{BuP}(\text{O})(\text{OBu})_2$ ,  $\text{Bu}_2\text{P}(\text{O})\text{OBu}$  and  $\text{Bu}_3\text{PO}$ . The results are shown graphically and tabularly at different concns. of the extractants in the hydrocarbon medium. Only  $\text{BuP}(\text{O})(\text{OBu})_2$  used at concn. above 50% in the hydrocarbon solvent shows a declining efficiency of extn. of  $\text{HNO}_3$ ; this is not shown by the other substances and no explanation for this phenomenon is given. The extrns were run from N  $\text{HNO}_3$  in the presence of 30 g./l. uranyl nitrate. Extn. with  $\text{Bu}_3\text{PO}$  in hydrocarbon system gave a 2nd organic layer evidently of a complex between  $\text{Bu}_3\text{PO}$  and  $\text{HNO}_3$ ; this was not observed if the org. fluid was  $\text{CCl}_4$ . At concn. range of 0-50% of the extractant in the org. phase, there is a decline of extn. of  $\text{HNO}_3$  in the presence of  $\text{UO}_2$  ion in passing from  $(\text{BuO})_3\text{PO}$  to  $\text{Bu}_3\text{PO}$ , this being caused by greater effectiveness of the C-P linked substances to extract U and to undergo a displacement of the sorbed  $\text{HNO}_3$  by the uranyl groups.

G.M. Kosolapoff.

Niobium analog of phosphonitrilic chloride.

I. V. Tananaev, G. B. Seifer and E. A. Ioneva (N.S. Kurnakov Inst. Gen. Inorg. Chem.), Doklady Akad. Nauk S.S.S.R. 127, 584-5 (1959).

Heating  $\text{NbCl}_5$  with large excess of  $\text{NH}_4\text{Cl}$  finally to  $250-60^\circ$  (removal of unreacted materials in vacuo at  $325^\circ$ ) gave a yellow-brown solid which is slowly hydrolyzed by  $\text{H}_2\text{O}$ . The substance is close to  $\text{NbNCl}_2$ ;  $d_{20}$  2.05. The thermogram of decompn. under A gave an endothermic effect at  $420-60^\circ$ , when  $\text{NbN}$  and  $\text{Cl}_2$  are formed. The substance is anisotropic and has very high n.

G.M. Kosolapoff.

# Synthesis of some triethylsiloxyalkoxytitanium compounds.

Organic

K. A. Andrianov and V. V. Astakhin. Doklady Akad. Nauk S.S.S.R. 127, 1014-5 (1959). cf. Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1958, 644.

Slow distn. of BuOH through a fractionating column from 105.6 g.  $\text{Et}_3\text{SiOH}$ , 136 g.  $\text{Ti}(\text{OBu})_4$  and 0.02 g. Na gave 34%  $(\text{BuO})_2\text{Ti}(\text{OSiEt}_3)_2$ ,  $b_4$  182°,  $d_{20}$  0.9517,  $n_D^{20}$  1.4758. Similarly, 68 g.  $\text{Ti}(\text{OBu})_4$  and 79.2 g.  $\text{Et}_3\text{SiOH}$  with 0.015 g. Na gave 90% BuOH and 46%  $(\text{Et}_3\text{SiO})_3\text{TiOBu}$ ,  $b_3$  174-7°, 0.9378, 1.4687. Similarly 113.6 g.  $\text{Ti}(\text{OPr})_4$  and 105.6 g.  $\text{Et}_3\text{SiOH}$  with 0.02 g. Na gave 95% PrOH and 21%  $(\text{PrO})_2\text{Ti}(\text{OSiEt}_3)_2$ ,  $b_{1.5}$  144-6°, 0.9680, 1.4800. Cf. Brown et al. JACS 79, 4616(1957).

G.M. Kosolapeff.

Organic

## Esters of thieboronic acids and some of their transformations.

B. M. Mikhailev, T. K. Kozminskaya, N. S. Fedotov and V. A. Derekhov (N. D. Zelinskii Inst. Org. Chem., Moscow). Doklady Akad. Nauk S.S.S.R., 127, 1023-6 (1959). cf. Izvest. Akad. Nauk SSSR, Otd. Khim. Nauk 1959, 172.

Refluxing 20.5 g.  $\text{PrBBR}_2$  and 23 g. BuSH 13 hrs. gave 90%  $\text{PrB}(\text{SBu})_2$ ,  $b_{13}$  149-50°,  $d_{20}$  0.9106,  $n_D^{20}$  1.4956. Similarly was prepd. 88.5%  $\text{BuB}(\text{SBu})_2$ ,  $b_7$  148-50°, 0.9045, 1.4936; 80% iso-AmB(OBu)<sub>2</sub>,  $b_6$  153.5-4°, 0.8988, 1.4871; 53% PhB(SBu),  $b_{1.5}$  137.5-8.5°, 0.9865, 1.5464; 69%  $\text{Ph}_2\text{BSBu}$ ,  $b_7$  178-80°, 1.001, 1.5871; 80%  $(1-\text{C}_{10}\text{H}_7)_2\text{BSBu}$ ,  $b_2$  245-7°. Heating 11.6 g. iso-AmB(SBu)<sub>2</sub> with 2.68 g.  $(\text{CH}_2\text{NH}_2)_2$  2 hrs. at 150° gave 90% BuSH and 85.5% 2-isoamyl-2-bora-1,3-diazolidine,  $b_{12}$  80-1°, 0.9165, 1.4872; this formed in 77% yield from 14 g. iso-AmBCl<sub>2</sub> and 11 g.  $(\text{CH}_2\text{NH}_2)_2$  in  $\text{Et}_2\text{O}$ .  $\text{PrB}(\text{SBu})_2$  similarly gave 83.5% 2-propyl-2-bora-1,3-diazolidine,  $b_{25}$  67-8°, 0.9406, 1.4941. Passage of  $\text{NH}_3$  over 40 min. into 10.3 g. iso-AmB(SBu)<sub>2</sub> gave 84.5% BuSH and 87.7% B-tri-isoamylborazol,  $b_{0.1}$  114-5.5°. Similarly PhB(SBu)<sub>2</sub> gave 95% B-triphenylborazol, m. 178-80°. Heating 9.9 g. PhB(SBu)<sub>2</sub> and 6.1 g.  $\text{Et}_2\text{NH}$  5 hrs. at 95° gave 80% PhB(NEt<sub>2</sub>)<sub>2</sub>,  $b_{2.5}$  115.5-6.5°, 0.9406, 1.5183.  $\text{Ph}_2\text{BSBu}$  and iso-BuNH<sub>2</sub> in 1 hr. gave 80.7%  $\text{Ph}_2\text{BNHCH}_2\text{CHMe}_2$ ,  $b_8$  161-3°, -, 1.560.  $\text{Ph}_2\text{BSBu}$  and  $\text{NH}_3$

2

gave in 1 hr. 85.4%  $\text{Ph}_2\text{BNH}_2$ , m.  $141-2^\circ$ . Similarly was prepd. 70%  $(1-\text{C}_{10}\text{H}_7)_2\text{BNH}_2$ , m.  $113-4^\circ$ .

G.M. Kosolapoff.



*Organic*

Synthesis and transformations of oxygen-containing organosilicon compounds.

8. Synthesis and properties of low molecular weight ethers of methyl- $\alpha$ -naphthylsilanediol.

M. F. Shostakovskii and Kh. I. Kondrat'ev (N. D. Zelinskii Inst. Org. Chem., Moscow). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1959, 1041-8.  
cf. 1956, 970.

Addn. of 31 g.  $\alpha$ -C<sub>10</sub>H<sub>7</sub>SiMeCl<sub>2</sub> (b<sub>1.5</sub> 123-5°, d<sub>20</sub> 1.2357, n<sub>D</sub><sup>20</sup> 1.6026) over 1.5 hrs. to 125 ml. H<sub>2</sub>O, 0.14 mole MgO and 130 ml. Et<sub>2</sub>O at 0° gave on evapn. of the org. layer 88.4% crude  $\alpha$ -C<sub>10</sub>H<sub>7</sub>SiMe(OH)<sub>2</sub> (I), contg. N(OSiMe-C<sub>10</sub>H<sub>7</sub>)<sub>n</sub>OH. This distd. with BuOH gave 20.3%  $\alpha$ -C<sub>10</sub>H<sub>7</sub>SiMe(OBu)<sub>2</sub>, b<sub>14-15</sub> 196-204°, b<sub>2-2.5</sub> 168-70°, 0.9987, 1.5270, 37.7% ( $\alpha$ -C<sub>10</sub>H<sub>7</sub>SiMe(OBu)<sub>2</sub>)<sub>2</sub>O, b<sub>14-15</sub> 297-312°, b<sub>2</sub> 238-44°, 1.0730, 1.5995, and 26.7% BuO(C<sub>10</sub>H<sub>7</sub>SiMeO)<sub>3</sub>Bu, b<sub>14-15</sub> 248-52°, b<sub>1.5-2</sub> 297-304°, 1.1183, -. Decreasing the amt. of BuOH tends to reduce the amts. of the ~~main~~<sup>less</sup> complex products, the main product being BuO(C<sub>10</sub>H<sub>7</sub>SiMeO)<sub>4</sub>H, b<sub>14-15</sub> 367-84°, b<sub>1.5-2</sub> 334-44°, 1.1448, -. Reaction of  $\alpha$ -C<sub>10</sub>H<sub>7</sub>SiMeCl<sub>2</sub> (228 g.) with BuONa (from 42 g. Na) in MePh at 11-19° gave 86%  $\alpha$ -C<sub>10</sub>H<sub>7</sub>SiMe(OBu)<sub>2</sub>, b<sub>2-2.5</sub> 166-72°, 0.9987, 1.5268, and 5-6% II. Addn. of 49 g. BuOH of 40 g.  $\alpha$ -C<sub>10</sub>H<sub>7</sub>SiMeCl<sub>2</sub> over 3 hrs. at room temp. in vacuo followed by 2 hrs. at 35-76° at 32-40 mm. gave 47 g. Cl-contg. product (III) which treated with BuONa gave some C<sub>10</sub>H<sub>8</sub>, 60%  $\alpha$ -C<sub>10</sub>H<sub>7</sub>SiMe(OBu)<sub>2</sub> and 11% II. Heating III with H<sub>2</sub>O gave no hydrolysis in 1 hr. at 120-30°; the result was the same in H<sub>2</sub>O-BuOH mixt.

G.M. Kosolapoff.

*Organic*

extractions isolation of pentavalent neptunium.

A.I. Alimarin, M. A. Golostov and M. A. Gal'shin (V.I. Vernadskii Geochem. and Anal. Chem. Inst.), Doklady Akad. Nauk SSSR, 124, 528-30 (1959).

$Np^V$  may be extd. by solns. of 1-nitroso-2-naphthol in BuOH or iso-amOH at pH 1-10. The work was explored with tracer quantities, then checked on gravimetric analysis. The necessary  $Np^V$  was formed by reduction of  $Np^{VI}$  with hydrazine. The extract and was adjusted to the desired pH with  $H_2O$ -HNO<sub>3</sub>. The optimal extractant for use as 1% soln. in the desired alc. Below pH 5 no extrn. takes place; the best extrn. occurs at pH 8-10 with 40-50% extrn. with BuOH in 1 extrn. with equal vols. of the 2 layers; iso-amOH gave 90-95% extrn., BuOH, CHCl<sub>3</sub> and  $CCl_4$  were less effective. At pH above 9-10 a ppt. of the extractant occurs with most solvents, but with BuOH this occurs only above pH 11.4. Reduction of extractant concn. in BuOH to 1% gives a useful solvent for extrn. and gives a cleaner liquid phase. Interferences are listed as:  $F^-$ ,  $CO_3^{--}$ ,  $PO_4^{---}$ ,  $NO_3^-$ , chlorate. A severe interference or hindrance is caused by ethyl-arsine, arsenic acid. Small amounts of fluorides or carbonates are not harmful. Nitrogen, chlorides or sulfates do not interfere. The extrn. depends on interaction of  $npO_2^-$  ion with the naphthol extractant. The procedure is useful for separ. of Np from U and Pu. Uranyl ion is not extd. at pH 3.5-4 (or above),  $Np^V$  is not extd.  $Pu^{IV}$  can be extd. at pH 1-1.5. Since it is possible to obtain solns. contg.  $U^{VI}$ ,  $Np^V$  and  $Pu^{IV}$ , (as for example with  $NaNO_2$ ), the possibility for separ. of these is evident.

A.I. Kosolapoff.

*Organic*

Effect of side chains on rate of oxidation of carbon chain polymers.

V.I. Yur'ev, A.A. Lavrenko and A. A. Sedukhin. Doklady Akad. Nauk SSSR, 124, 355-57 (1959).

Direct action of  $O_2$  at 135-245° was examined with specimens: rene, polymethylene, polymeric hydrocarbons with side-chain

decompn. of diazomethane, diazobutane, diazoethane., and poly-p-isopropylstyrene. The kinetic curves are reproduced. In general, side-chains are sites for active oxidation and their presence increases  $O_2$  uptake very considerably. The aliphatically branched polymers show evidence of some cross linking during the oxidation, this being evidently caused by O-bridging during the radical reaction. Polystyrene did not show this behavior in the group of polymers studied.

G.M. Kosolapoff.

*Organic*

Synthesis of ferrocene derivatives with N,N-diethylaminomethylferrocene methiodide.

A.A. Cheshevov, E.G. Perevalova, L.S. Shilovtseva and Yu.A. Ustynvuk (A.V. Lomonosov State Univ., Moscow). Doklady Akad. Nauk SSSR, 124, **331-34** (1959) (I)  
 Heating 1.1 g. N,N-diethylaminomethylferrocene methiodide and 1.5 g.  $Na_2SO_4 \cdot 7H_2O$  in 60 ml.  $H_2O$  7 hrs. at  $80^\circ$ , treatment with  $Na(OH)_2$ , removal of excess  $Na$  with  $CO_2$ , concn. of the filtrate, gave 77% Na ferrocenylmethanesulfonate monohydrate, crystals (from  $H_2O$  or EtOH), does not m.  $230^\circ$ . I and aq. KOH in 3 hrs. of reflux gave 46% ferrocenylmethyl thiocyanate, m.  $59-61^\circ$  (from petr. ether). I with PhOH and NaOH in 5 hrs. at  $80-90^\circ$  gave after usual ac. treatment 30% phenyl ferrocenylcarbinol ether, m.  $189-30^\circ$  (from petr. ether). Similarly was prepd. 3-naphthyl ferrocenylcarbinyl ether, dec.  $121-23^\circ$  (from petr. ether). To 0.5 g. p-HOC<sub>6</sub>H<sub>4</sub>Me in 5% NaOH was added aq. soln. of 1 g. I and after 30 hrs. at  $100^\circ$  there formed a ppt. of 80% p-ferrocenylmethoxyazobenzene, dec.  $155.5-37.5^\circ$  (from  $C_3H_6$ ). To 20.8 g. Et<sub>2</sub>NH in 50 ml. AcOH was added 6.4 g. paratolaldehyde and 18.0 g. ferrocene; after 16 hrs. at  $80-100^\circ$ , this was dild. with  $H_2O$ , filtered from unreacted ferrocene, the aq. soln. made alkaline and extd. with Et<sub>2</sub>O, yielding some 2g. steamdistillable N,N-diethylaminomethylferrocene, isolated as methiodide, dec.  $159-62^\circ$  (from EtOH). Heating 30 g. methyl-

5

ferrocene, 15.3 g.  $\text{CH}_2(\text{NMe}_2)_2$ , 4.5 g. paraformaldehyde, 30 g.  $\text{H}_3\text{PO}_4$  (D. 1.73) and 200 ml. AcOH 7 hrs. at  $95^\circ$  gave after distn. of the products in vacuo over Zn dust 80% N,N-dimethylaminomethyl-methylferrocene,  $b_1$   $115-18^\circ$ ,  $b_5$   $138-40^\circ$ ,  $n_D^{20}$  1.5612,  $d_{20}$  1.2150 (infra red spectrum is indicated), and 19% bis-(N,N-dimethylaminomethyl)-methylferrocene,  $b_1$   $130-31.5^\circ$ , 1.5622, 1.1260 (infrared spectrum indicated). The former yields the methiodide,  $\text{dec. } 185^\circ$  (from MeOH-Et<sub>2</sub>O). If the  $\text{H}_3\text{PO}_4$  is omitted, the yield of the mono-deriv. is 60% (74% if isolated as the methiodide). If the reaction is run at  $110-15^\circ$  10 hrs. the yield of the mono-deriv. is 42% and that of disubstituted product is 32%. Reduction of II with Na-Hg gave 75% dimethylferrocene,  $b_4$   $77^\circ$ ,  $b_{13}$   $119^\circ$ , 1.6007, 1.2458,  $n_D^{25}$  1.5922 (infrared spectrum indicated). The spectrum indicates that the product is homoannular and that the Me groups are probably in 1,3-positions.

Fluoroorganosilicon compounds. Addition reaction of alkylchlorosilicon hydrides to 1,1,2,2-tetrafluoroethyl allyl ether.

A. D. Petrov, V. A. Ponomarenko, G. V. Babashyan and S. I. Krokhmalev  
(N. D. Zelinskii Inst. Org. Chem., Moscow). Doklady Akad. Nauk SSSR, 124, 838-41 (1959). Cf. 121, No.2 (no pp) (1958).

Heating 40.6 g.  $\text{Cl}_3\text{SiH}$  with 47.5 g.  $\text{CH}_2:\text{CHCH}_2\text{OCF}_2\text{CF}_2\text{H}$  at  $161^\circ$  with 0.3 g. 1% Pt-C 3 hrs. in autoclave gave 58%  $\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{H}$ ,  $b_{751} 186^\circ$ ,  $d_{20} 1.4335$ ,  $n_D^{20} 1.3994$ . Similarly were obtained:  $\text{Cl}_2\text{SiMeCH}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{H}$ , 35%,  $b_{750} 190.1^\circ$ , 1.3140, 1.3960;  $\text{Cl}_2\text{SiEtCH}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{H}$ , 63%,  $b_{749} 207.2^\circ$ , 1.2837, 1.4033; 40%  $\text{Cl}_2\text{SiPrCH}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{H}$ ,  $b_{11} 101^\circ$ , 1.2484, 1.4062; and 46%  $\text{MeEtClSiCH}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{H}$ ,  $b_{749} 199^\circ$ , 1.1681, 1.3956. Reaction of  $\text{MeEt}_2\text{SiH}$  and the above ether occurred exothermically in iso-PrOH when  $\text{H}_2\text{PtCl}_6$  soln. was added to the components and gave in 30 min. 28%  $\text{MeEt}_2\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{H}$ ,  $b_{749} 196.5^\circ$ , 1.0422, 1.3930. The above halogen derivs. gave with  $\text{MeMgBr}$ : 58.9%  $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{H}$ ,  $b_{746} 156^\circ$ , 1.0453, 1.3732; 67.5%  $\text{Me}_2\text{EtSiCH}_2\text{CH}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{H}$ ,  $b_{739} 176^\circ$ , 1.0402, 1.3830; 57.3%  $\text{Me}_2\text{PrSiCH}_2\text{CH}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{H}$ ,  $b_{751} 193^\circ$ , 1.0267, 1.2886.  $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OH}$  was treated with Na and the product heated in autoclave with  $\text{CF}_2:\text{CF}_2$  at 10 atm. gave 48.7%  $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{H}$ , identical with the above.  $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{OH}$  similarly gave 21.6%  $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{H}$ ,  $b_{746} 137^\circ$ , 1.0427, 1.3732.

*Organic*

## Reactions of hexafluoro-1,3-butadiene with alcohols and amines.

I.L.Knunyants, B.L.Dyatkin and L.S.German (Inst. Hetero-Org. Compounds, Moscow). Doklady Akad. Nauk SSSR, 124, 1065-68 (1959).

(I)  
 Keeping 21 g. hexafluoro-1,3-butadiene in 200 ml. abs. EtOH contg. 4.8 g. Na with ice cooling 1 day gave, after quenching in dil. HCl and washing, an oil which evolved some HF during distn. and yielded 18.9 g. product with  $b_{17}$  45-83°. Treated with silica gel, this evolved more HF with heat evolution. On the following day the product was taken up in Et<sub>2</sub>O, washed with H<sub>2</sub>O and distd. yielding 41.8% 1,4-diethoxyperfluoro-1,3-butadiene,  $b_{17}$  83-85°,  $n_D^{20}$  1.3871,  $d_{20}$  1.1883 (Infrared spectrum shows a band at 1740 cm<sup>-1</sup>). This (9 g.) in 20 ml. CH<sub>2</sub>Cl<sub>2</sub> was treated over 2 hrs. with 2.5 ml. concd. H<sub>2</sub>SO<sub>4</sub> and after shaking several hrs. and standing overnight, the mixture yielded after an aq. treatment 83.6% di-Et fluoroethylenedicarboxylate, EtO<sub>2</sub>CCF:CH-CO<sub>2</sub>Et,  $b_{1.5}$  74°, 1.4330, 1.1456. I (16.2 g.), 6 ml. dry ~~Et~~ NaOH and 0.8 ml. Et<sub>3</sub>N were heated 4 hrs. at 90-100° in steel ampul; after treatment with dil. HCl there was obtained 50% 1-methoxyhydroperfluoro-2-butene, MeOCF<sub>2</sub>CF:CFCH<sub>2</sub>F,  $b_{143}$  30-31°, 1.3030, 1.3696 (infrared spectrum has a band at 1700 and 1730 cm<sup>-1</sup>). Similarly EtOH gave 53.5% EtC analog,  $b_{144}$  48.5°, 1.3270, 1.3090 (infrared spectrum has bands at 1730 and 1790 cm<sup>-1</sup>). Addn. of 16.2 g. I with ice cooling to 18 g. Et<sub>2</sub>NH in Et<sub>2</sub>O over 0.5 hr., stirring 1 hr., followed by filtration and distn. under N<sub>2</sub> gave 81% 1-diethylaminoperfluoro-1,3-butadiene,  $b_{15}$  45°, 1.3960, -, containing 9.29% hydrolyzable F (infrared spectrum has bands at 1710 and 1800 cm<sup>-1</sup>). This shaken in Et<sub>2</sub>O with H<sub>2</sub>O a few minutes gave 86% CF<sub>2</sub>:CFCHCONEt<sub>2</sub>,  $b_{3.5}$  63.5°, 1.4110, 1.2428 (infrared spectrum has bands at 1660 and 1800 cm<sup>-1</sup>). Reaction of I with piperidine in Et<sub>2</sub>O, run as above, gave ~~12%~~ after an aq. treatment 48% CF<sub>2</sub>:CFCHCON(CH<sub>2</sub>)<sub>5</sub>,  $b_5$  94°, 1.4420, 1.3203 (infrared spectrum has bands at 1660 and 1800 cm<sup>-1</sup>). Similar reaction of I with EtNH<sub>2</sub> in Et<sub>2</sub>O gave after treatment with ice-HCl a low yield of EtNHCOCF:CHCONHEt, m. 195° (from Et<sub>2</sub>O) and a little CF<sub>2</sub>:CF-CHCONHEt, m. 55-56° (from octane).

G.M.Kosolapoff.

aq. KI gave after a steam distn. 80.9% 2,4-difluoroiodobenzene, b. 175-5°,  
 $b_{25}^{75^\circ}$ ,  $n_D^{20}$  1.5574. Bromination of  $m\text{-C}_6\text{H}_4\text{F}_2$  in the presence of Fe gave  
 after 1 day at room temp. 70.7% 2,4-difluorobromobenzene, b. 145-46°,  $n_D^{20}$   
 1.5059. This was converted to the Grignard reagent by reaction with Mg  
 in the presence of equimolar amount of EtMg by entrainment method; the  
 soln. was treated with  $\text{CoCl}_2$  under  $\text{H}_2$  and finally treated with  $\text{CH}_3\text{COCl}$   
 at 0°, warmed to room temp. for 2 hrs. and quenched in ice-HCl, yielding  
 5% 2,4-difluorostyrene which was isolated only as the dibromide, which was  
 identical with the one described above,  $b_{10}^{111-15^\circ}$ . G.M. Kosolapeff.

2. 2,4-Difluoro- $\beta$ -fluorostyrene <sup>Organic</sup> and 2,4-difluoro- $\beta\beta$ -difluorostyrene.

Ibid. 71-75.

Bromination of 2,4-difluoroacetophenone at 0°, finally 4 hrs. at room temp.,  
 gave 90.7% 2,4-difluoro- $\beta\beta$ -dibromoacetophenone,  $b_2^{104-105^\circ}$ . This (62.8 g)  
 was added dropwise over 3 hrs. at 160° and 16 mm. to a soln. prepd. from  
 51.8 g. KF and 170 ml. dry glycerol (heated 0.5 hr. at 160° under gradually  
 improving vacuum); further heating to 185° at 9-10 mm. gave a distillate  
 of 10% 2,4-difluoro- $\beta\beta$ -difluoroacetophenone,  $b_{25}^{91-92^\circ}$ ,  $n_D^{20}$  1.4694;  
 this was obtained in 48.3% yield by treatment of 2,4- $\text{F}_2\text{C}_6\text{H}_3\text{Br}$  in  $\text{Et}_2\text{O}$  at  
 -75° with ethereal BuLi soln., followed by  $\text{F}_2\text{CHCO}_2\text{H}$ , stirring 10 min. and  
 quenching in ice; the product,  $b_{25}^{90-90.5^\circ}$ ,  $n_D^{20}$  1.4694. Reduction of this  
 with  $\text{NaBF}_4$  in aq. NaOH-MeOH gave after 1 hr. at under 50° and quenching in  
 aq. NaOH, 90.2% 2,4-difluorophenyl difluoromethylcarbinol,  $b_{24}^{105^\circ}$ ,  $n_D^{20}$   
 1.4582, which with  $\text{SOCl}_2$ -pyridine at below 25°, finally 1 hr. at 80°, gave  
 after an aq. treatment 78.8% 2,4- $\text{F}_2\text{C}_6\text{H}_3\text{CHClCHF}_2$ ,  $b_{25}^{81-83^\circ}$ ,  $n_D^{20}$  1.4606.  
 This (18.3 g.) heated carefully with 0.35 g. powd. Cu, 6.15 g. Zn dust  
 and 26 g.  $\text{AcNH}_2$  to 85°, then 120° 0.5 hr. gave after quenching in aq.  $\text{NH}_3$ ,  
 88.2% 2,4- $\text{F}_2\text{C}_6\text{H}_3\text{CH:CHF}_2$ ,  $b_{40}^{65-67^\circ}$ ,  $n_D^{20}$  1.4800. Reaction of 230 ml. 0.1N  
 BuLi in  $\text{Et}_2\text{O}$  with 38.6 g. 2,4- $\text{F}_2\text{C}_6\text{H}_3\text{Br}$  and 13 g.  $\text{F}_2\text{CHCO}_2\text{H}$  as above gave  
 45% 2,4- $\text{F}_2\text{C}_6\text{H}_3\text{COOClF}_2$ ,  $b_{35}^{98-99.5^\circ}$ ,  $n_D^{20}$  1.4685; the same formed in 22.2%

3  
 yield from  $m\text{-C}_6\text{H}_4\text{F}_2$  and  $\text{AcCl}$ , in the presence of  $\text{AlCl}_3$ , in  $\text{CS}_2$ ;  $b_{35}$   $94-95^\circ$ ,  
 $n_D^{20}$  1.4683, along with a fraction,  $b_{45}$   $64-65.5^\circ$ . The ketone treated with  
 $\text{NaBF}_4$  in aq.  $\text{NaOH-MeOH}$  gave 83.7%  $2,4\text{-F}_2\text{C}_6\text{H}_3\text{OH}(\text{OH})\text{OOCF}_2$ ,  $b_{35}$   $112-113.5^\circ$ ,  
 $n_D^{20}$  1.4642, which with pyridine- $\text{SOCl}_2$ , finally at  $78-80^\circ$  0.5 hr., gave  
 57.7%  $2,4\text{-F}_2\text{C}_6\text{H}_3\text{CHClCOClF}_2$ ,  $b_{35}$   $95-97^\circ$ ,  $n_D^{20}$  1.4589, which heated with  $\text{Zn}$   
 dust in  $\text{AcNH}_2$  at  $120-30^\circ$  2.5 hrs. gave after quenching in aq.  $\text{H}_2\text{SO}_4$  and  
 extrn. with  $\text{Et}_2\text{O}$ , 38.2%  $2,4\text{-F}_2\text{C}_6\text{H}_3\text{CH:OFCF}_2$ ,  $b_{60}$   $62^\circ$ ,  $n_D^{20}$  1.4545.

G.M. Kosolapoff.



*Organic*

Condensation of vinylcyclohexene with propiolic and tetrolic acids and their esters.

I. N. Nazarov, S. N. Ananchenko and I. V. Torgov (N. D. Zelinskii Inst. Org. Chem., Moscow ). Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk, 1959, 95-102.

Stirring 500 g. 1,3-dichloro-2-butene with 1 l.  $H_2O$  and 380 g. powd.  $CaCO_3$  12 hrs. at  $70-80^\circ$  gave after extn. with  $Et_2O$  61% 3-chloro-2-buten-1-ol, (I),  $b_{12}$   $65-69^\circ$ ,  $n_D^{20}$  1.4650. To 200 g. powd. KOH in 320 ml. abs. EtOH was added at room temp. with stirring 250 g. I and after 4.5 hrs. at  $100^\circ$ , standing overnight, dila. with 300 ml. EtOH, neutralization with  $CO_2$ , filtration, acidification of the filtrate with HCl, refiltration and distn., there was isolated 71% 2-buten-1-ol, b.  $140-45^\circ$ ,  $n_D^{20}$  1.4550. This (31 g.) in 220 ml.  $Me_2CO$  was ~~stirred~~ <sup>treated</sup> over 1.5 hrs. with 63 g.  $CrO_3$  in 30%  $H_2SO_4$ , stirred 5 hrs. and left overnight; after extn. with  $Et_2O$ , 48% tetrolic acid, m.  $76-77^\circ$ ,  $b_{16}$   $96-100^\circ$ , was isolated. This refluxed with MeOH in the presence of  $H_2SO_4$  16 hrs. gave the Me ester, b.  $85$   $30-32^\circ$ ,  $n_D^{19}$  1.4408.  $C_2H_2$  was introduced into soln. of 46 g. Na in 1.5 l. liq.  $NH_3$  until the color was discharged, after which 500 ml.  $Et_2O$  was added,  $NH_3$  was evaporated, finally in  $H_2$  stream, and the resulting suspension of  $NaNH_2$  in  $Et_2O$  was treated with  $CO_2$  at 25-30 atm. in autoclave 72 hrs. at room temp., yielding after aq. treatment and acidification 52% propiolic acid, b.  $50$   $80-88^\circ$ , which with MeOH- $H_2SO_4$  in 2 days at room temp. gave the Me ester, b.  $102^\circ$ . Refluxing 4.5 g. 1-vinylcyclohexene (II) with 3.7 g. Me propiolate in MePh 9 hrs. gave 85% (based on conversion) mixed Me  $\Delta^{1,4}$ -hexahydronaphthalene-1-carboxylate and -2-carboxylate, b.  $8$   $124-25^\circ$ ,  $n_D^{20}$  1.5170,  $d_{20}$  1.065. Refluxing 10.4 g. II with 8 g. propiolic acid in dioxane 10 hrs. gave 5 g. pure  $\Delta^{1,4}$ -hexahydronaphthalene-1-carboxylic acid, m.  $137-38^\circ$ ,  $\lambda_{max}$  246 m $\mu$ ; the mother liquor gave 5.5 g. crystals, m.  $88-95^\circ$ , of mixed acids which could not be sepd. and after many recrystallizations gave merely the constant melting mixture of the 1- and 2-carboxy isomers, m.  $96-98^\circ$ . Very slow

crystallization of this from petr. ether ( very dil. soln. ) gave the 1-carboxylic acid, needles, m. 136-37°, and the 2-carboxylic acid, plates, m. 129-30°,  $\lambda_{\max}^{246} m\mu$ , which were sepd. mechanically. Hydrolysis of the mixed Me esters ( above ) with aq. NaOH gave the same isomeric acids, which were sepd. as above. Esterification of the 1-carboxylic acid with  $CH_2N_2$  gave its Me ester, b<sub>1.5</sub> 91-1.5°,  $n_D^{22}$  1.5145, which on saponification with aq. NaOH gave the original acid, m. 137-38°. Hydrogenation of the pure  $\Delta^{1,4}$ -hexahydronaphthalene-1-carboxylic acid over Pt in MeOH gave cis-syn-decahydronaphthalene-1-carboxylic acid, m. 124-25°; the same formed over Pd-CaCO<sub>3</sub>, or over Pt in AcOH. The acid treated with  $[COCl]_2$ , followed by NH<sub>3</sub>, gave the amide, m. 235-36°. Similar hydrogenation of  $\Delta^{1,4}$ -hexahydronaphthalene-2-carboxylic acid gave cis-trans-decahydronaphthalene-2-carboxylic acid, m. 80.5-81°; amide, m. 178-79° ( from EtOH ); ~~with EtOH~~ the acid treated in CHCl<sub>3</sub> with H<sub>2</sub>SO<sub>4</sub> and NaN<sub>3</sub>, followed by BzCl in the presence of NaOH, gave the N-benzoylamide, m. 128-29°. Reduction of  $\Delta^{1,4}$ -hexahydronaphthalene-1-carboxylic acid with LiAlH<sub>4</sub> on Et<sub>2</sub>O overnight gave after the usual treatment 76% 1-hydroxymethyl- $\Delta^{1,4}$ -hexahydronaphthalene, m. 50-51°, which ( 1 g. ) treated with 0.7 g. powd. K<sub>2</sub>CO<sub>3</sub> and 0.6 g. PBr<sub>3</sub> in petr. ether at -70°, then at room temp. overnight, gave 1.2 g. 1-bromomethyl analog, a strong lachrymator,  $n_D^{20}$  1.5480; this condensed with sodio-malonic and -acetoacetic esters, but the products were unstable; the reaction failed to go with sodioacetone. Heating 7.8 g. II with 7.8 g. Me tetrolate in dioxane 3 hrs. at 130° in autoclave gave 3.2 g. mixed condensation products, b<sub>3</sub> 107-18°. This refluxed 10 hrs. with MeOH-KOH gave after acidification 0.4 g. 2-methyl- $\Delta^{1,4}$ -hexahydronaphthalene-1-carboxylic acid, m. 165-66°; some dimer of II was also isolated, b<sub>5</sub> 139-40°. Heating II with tarolic acid in dioxane as above gave after recrystallization from Me<sub>2</sub>CO a low yield of pure 2-methyl- $\Delta^{1,4}$ -hexahydronaphthalene-1-carboxylic acid, m. 166.5-67°; Keeping 0.3 g. 1-vinyl-6-methoxy-5,4-dihydronaphthalene and 0.16 g. propiolic acid in dioxane 2 hrs., then refluxing 3 hr. gave 80% mixed acids which after evaporation from dioxane on a 0 gave

**Synthesis of methylecrotonamide.**

*Organic*

S. N. Ushakov, E. M. Lavrent'eva and K. S. Podgorskaya (High Polymer Inst., Leningrad ). Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk, 1959, 91-94.

The following conditions were found to be best from the synthesis of methylecrotonamide. Equimolar amounts of crotonamide and paraformaldehyde were made to react in the presence of 2.5-3% EtONa at 68-70° 15-20 min. in CCl<sub>4</sub> soln. with stirring; the upper layer was sepd., filtered and chilled overnight, yielding 62-85% MeCH:CHCONHCH<sub>2</sub>OH, needles, m. 87° ( from EtOAc or C<sub>6</sub>H<sub>6</sub> ), n 1.5160. Heated in aromatic solvent with distn. of H<sub>2</sub>O with the solvent vapors it formed the ether (MeCH:CHCONHCH<sub>2</sub>)<sub>2</sub>O, m. 136°, n<sub>D</sub><sup>20</sup> 1.5557, n 1.5540, d<sub>20</sub><sup>20</sup> 1.1312.

G.M. Kosolapoff.

*Organic*



2

80.2%

~~Et<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>SCN~~ Me<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>SCN, b<sub>5</sub> 147-48°, 1.4774, 0.9371; 84.8%  
 Et<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>SCN, b<sub>5</sub> 152°, 1.4869, 0.9365; 83% PrMe<sub>2</sub>Si(CH<sub>2</sub>)<sub>3</sub>SCN, b<sub>5</sub> 139°, 1.4790, 0.9241; 79.9% Me<sub>2</sub>PhSi(CH<sub>2</sub>)<sub>3</sub>SCN, b<sub>9</sub> 208°, 1.5360, 1.-144  
 97% EtMe<sub>2</sub>Si(CH<sub>2</sub>)<sub>3</sub>SCN, b<sub>6</sub> 153.5°, 1.4802, 0.9251; 72% MeEt<sub>2</sub>Si(CH<sub>2</sub>)<sub>3</sub>SCN, b<sub>5</sub> 162.5°, 1.4823, 0.9278; MeCl passed into Et<sub>2</sub>O with 75 g. Mg  
 16 hrs., followed by addn. of 252 g. MeSiCl<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Cl and reflux 8 hrs.  
 gave after an aq. treatment 83.4% ClCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiMe<sub>3</sub>, b<sub>740</sub> 150°, 1.4320, -.  
 This with EtSiMe<sub>2</sub> in Et<sub>2</sub>O gave in 40 hrs. 74.3% Me<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>SEt, b<sub>7</sub> 70-71°, 1.4581, 0.8479. The same formed from Me<sub>3</sub>SiCH<sub>2</sub>CH:CH<sub>2</sub> and EtSiMe<sub>2</sub> in 10 days' standing (60.5%). Hydrolysis of Me<sub>3</sub>SiCH<sub>2</sub>CHMeSP(S)(OMe)<sub>2</sub> gave Me<sub>3</sub>SiCH<sub>2</sub>CHMeSO<sub>2</sub> whose infra-red spectrum was quite different from that of the above isomer. Trialkylalkenylsilanes and S yield mixed polysulfides.

G.M. Kosolapoff.

**Emanating ability in topochemical processes as a characterization of specific surface.**

**M. D. Sinitsyna, G. M. Zhabrova, S. Z. Roginskii and V. A. Gerdieva ,  
Invest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 176-78.**

**A specimen of  $Mh(OH)_2$  containing radiothorium was subjected to heating from  $320^\circ$  to  $1080^\circ$  with detn. of evolved  $H_2O$  and estn. of the emanating ability by detn. of the evolved thoron. It was shown that a linear dependence exists between the emanation coeff. and the specific surface of the specimen used. This suggests the use of such procedures for estn. of specific surfaces of solids in place of the sorptional methods.**

**G.M.Kosolapoff.**

*Organic*

**Polymerization of vinyl- and allyl derivatives of IV group elements.**

V. V. Kershak, A. M. Polyakova, V. P. Mironov and A. D. Petrov (Inst. Hetero-org. Compds., Moscow). Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk, 1959, 175-80.

Cf. this j. 1956, 980, and Zhur. Obshch. Khim. 27, 2445 (1957).

Heating  $\text{Me}_3\text{SiCH:CH}_2$  6 hrs. at  $120^\circ$  under 6000 atm. in the presence of  $(\text{Me}_3\text{CO})_2$  gave a liquid polymer of low mol. wt., comparable to that formed by  $\text{Me}_3\text{COH:CH}_2$ .  $\text{Me}_3\text{SiCH}_2\text{CH:CH}_2$  also gave a low mol. wt. polymeric oil;  $\text{Me}_3\text{-GeCH:CH}_2$  gave a similar result as did  $\text{Me}_3\text{GeCH}_2\text{CH:CH}_2$  and  $\text{Et}_3\text{SnCH:CH}_2$ .  $\text{Et}_3\text{SnCH}_2\text{CH:CH}_2$  failed to polymerize, while  $\text{Me}_2\text{Et}_2\text{Ge}(\text{CH:CH}_2)_2$  gave a good yield of tridimensional glassy polymer. Under the same conditions copolymers were formed from styrene and  $\text{Me}_3\text{GeCH}_2\text{CH:CH}_2$ , and  $\text{CH}_2\text{:CHCO}_2\text{Me}$  and  $\text{Me}_3\text{SnCH}_2\text{CH:CH}_2$  or  $\text{Me}_3\text{GeCH}_2\text{CH:CH}_2$ . Among vinyl and allyl derivs., those of Si polymerize better than do those of C, Ge or Sn; for derivs. of thiocyanate radical and the above elements, the ease of polymerization rises steadily from C to Si to Ge and to Sn, respectively.

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*Organic*

<sup>est</sup>  
 Hetero-chain polymers. 12. Polyesters of azobenzenes-3,3'- and 4,4'-dicarboxylic acids.

V. V. Korshak and S. V. Vinogradova (Inst. Hetero-org. Compds., Moscow).  
 Invest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 148-53. Cf. this j. 1957, 993.  
 Esterification of  $(:\text{HC}_6\text{H}_4\text{CO}_2\text{H}-m)_2$  with  $\text{MeOH}-\text{HCl}$  gave the di-Me ester, 20%,  
 m. 161-63°. The p-isomer failed to react under these conditions and required  
 the reaction of the acyl chloride with  $\text{MeOH}$ ; the di-Me ester, m. 240-41°, was  
 obtained in unstated yield. These esters were polycondensed in the presence  
 of  $\text{LiOH}$  with aliphatic glycols ranging from  $\text{C}_2$  to  $\text{C}_{20}$ , including also  
 propylene glycol and diethylene glycols. The polyesters from the m,m'-isomer  
~~mixtures~~ were generally low-melting solids, while those from the p,p'-  
 isomer generally melted well above 150°. The polyesters from the m-isomer  
 could be drawn into filaments, while those from the p-isomer could not.  
 The range of m.pt. of the resulting polyesters is discussed at length  
 from the viewpoint of electronic organic theory,

G.M. Kosolapoff.

13. Polyesters of p-xylylene glycol.

Ibid. 154-161.

*Organic*

Polyesters were prepd. from  $p\text{-C}_6\text{H}_4(\text{CH}_2\text{OH})_2$  and dicarboxylic acids: oxalic  
 through sebacic, as well as hexadecanedioic, diglycolic, thiodivaleric,  
 sulfonyldivaleric, isomeric  $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ , diphenyldicarboxylic, diphenic,  
 2,5-dimethylterephthalic, diphenylmethane-3,3'- and 4,4'-dicarboxylic,  
 diphenylketo-4,4'-dicarboxylic, p-phenylenediacetic, and trans- and cis-  
 hexahydroterephthalic acids. These were solids whose m.pt. ranged up to  
 over 240° for the terephthalic acid ester from as low at 28° for cis-hexa-  
~~hydroterephthalic~~ <sup>raph</sup> hydroterephthalic acid ester. The necessary glycol was prepd.  
 by hydrolysis of the bromide with aq.  $\text{K}_2\text{CO}_3$ . The polyesterifications were  
 run with 0.2-0.5%  $\text{LiOH}$  as the catalyst. The M.pt. and solys. of the products  
 are tabulated and compared with each other at some length.

G.M. Kosolapoff.



# Synthesis of organomercury nitro compounds.

*Organic*

S. S. Nevikov, T. I. Gedeonova and V. A. Tartakovskii (M. D. Zelinskii Inst. Org. Chem., Moscow). Doklady Akad. Nauk SSSR, 124, 834-37 (1959). It was shown that  $\text{Hg}[\text{C}(\text{NO}_2)_3]_2$  readily mercurates compds. with active H in  $\text{Et}_2\text{O}$ ,  $\text{H}_2\text{O}$ ,  $\text{C}_6\text{H}_6$ ,  $\text{EtOH}$ , or  $\text{MePh}$  at 20-30°, the reaction being quite rapid in most cases, or requiring up to 60 hrs. for less reactive cases. The products are evidently  $\text{RHgC}(\text{NO}_2)_3$  (R shown):  $\text{CH}(\text{CO}_2\text{Et})_2$ , dec. above 250°;  $\text{AcCHCO}_2\text{Et}$ , m. 159°;  $\text{O}_2\text{NCHCO}_2\text{Et}$ , m. 135°;  $\text{CH}(\text{CO}_2\text{Me})_2$ , m. 138°;  $\text{AcCH}_2$ , m. 155°; cyclopentanonyl, m. 140°; Ph, 146°,  $\text{MeC}_6\text{H}_4$  (p-, m. 149°; o-, m. 126°);  $\text{MeOC}_6\text{H}_4$  (p-, m. 101°; o- m. 114°);  $\text{PhNH}$ , m. 117°; p- $\text{Me}_2\text{NC}_6\text{H}_4$ , m. 110°; furyl, m. 120°; thienyl, m. 115°. With  $\text{Br}_2$  these give  $\text{RBrC}(\text{NO}_2)_3$  and corresponding mercurobromides; concd.  $\text{HCl}$  yields  $\text{RHgCl}$  and  $\text{HC}(\text{NO}_2)_3$ . The spectra of the products depend on the solvent polarity indicating the possible existence in 2 tautomeric forms in soln. Reaction with aryl nitro compounds does not yield such products but rather adducts, such as:  $\text{O}_2\text{NPh.Hg}[\text{C}(\text{NO}_2)_3]_2$ , m. 116°; m- $(\text{O}_2\text{N})_2\text{C}_6\text{H}_4.\text{Hg}[\text{C}(\text{NO}_2)_3]_2$ , m. 147°; o- $\text{Me}(\text{O}_2\text{N})-\text{C}_6\text{H}_4.\text{Hg}[\text{C}(\text{NO}_2)_3]_2$ , m. 75°; o- $\text{MeO}(\text{O}_2\text{N})\text{C}_6\text{H}_4.\text{Hg}[\text{C}(\text{NO}_2)_3]_2$ , m. 109°. Alkalies destroy these complexes and give the original  $\text{R}$ -nitroaromatic compd.,  $\text{HgO}$  and salt of  $\text{CH}(\text{NO}_2)_3$ . Products of neither nature are formed from m-substituted nitro compounds, this indicating that the above complexes are additively linked at m-position relative to  $\text{NO}_2$ . Reaction of  $\text{Hg}[\text{C}(\text{NO}_2)_3]_2$  with  $\text{C}_6\text{H}_4$  in aq. or alc. medium gave  $(\text{O}_2\text{N})_3\text{CCH}_2\text{CH}_2\text{HgC}(\text{NO}_2)_3$ ; the same forms in  $\text{NaNO}_2$  or  $\text{PhNO}_2$  soln. Reaction with phenylcyclopropane gave  $\text{PhCH}(\text{CH}_2)_2\text{CH}_2\text{HgC}(\text{NO}_2)_3$ , while reaction with  $\text{EtOCH}:\text{CH}_2$  gave  $(\text{O}_2\text{N})_3\text{CCH}_2\text{CH}_2\text{CHO}$  m. 128°, 65%.  $\text{RHgC}(\text{NO}_2)_3$  also add to the double bonds. Thus were prepd.:  $(\text{O}_2\text{N})_3\text{CCH}_2\text{CH}_2\text{HgC}(\text{NO}_2)_3$ , 93%, m. 167°;  $(\text{O}_2\text{N})_3\text{CCH}_2\text{CH}_2\text{HgCl}$ , 92%, m. 142°;  $(\text{O}_2\text{N})_3\text{CCH}_2\text{CH}_2)_2\text{Hg}$ , m. 155°;  $(\text{O}_2\text{N})_3\text{CCHMeCH}_2\text{HgC}(\text{NO}_2)_3$ , 97%, m. 124°;  $[(\text{O}_2\text{N})_3\text{CCHMe}-\text{CH}_2]_2\text{Hg}$ , 79%, m. 124°;  $(\text{O}_2\text{N})_3\text{CCHPhCH}_2\text{HgC}(\text{NO}_2)_3$ , m. 129°, 60%; o- $(\text{O}_2\text{N})_2\text{C}_6\text{H}_4-\text{HgC}(\text{NO}_2)_3$ , 55%, m. 95°;  $[(\text{O}_2\text{N})_3\text{CCH}(\text{CH}_2\text{OH})\text{CH}_2]_2\text{Hg}$ , 70%, m. 109°; and  $(\text{O}_2\text{N})_3\text{C}-\text{CH}_2\text{CH}(\text{CO}_2\text{Me})\text{HgC}(\text{NO}_2)_3$ , 82%, m. 150°. Iso-olefins do not add these Hg salts.

G.M. Kosolapoff.

Organic

Exchange reactions of isopropenyl compounds of mercury, thallium and tin.  
 A. N. Nesmeyanov, A. E. Borisov<sup>V</sup> and N. V. Novikova. (Inst. Hetero-org. Compds., Moscow). Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 259-62.

Exchange reactions of isopropenyl derivs. of Hg, Tl and Sn are described. Rapid heating of 5 g.  $(\text{CH}_2:\text{CMe})_2\text{TlBr}$  and 10 g.  $\text{SnBr}_2$  at  $200^\circ$  gave a distillate of 75% malodorous liquid, which on redistn. gave 2.2 g.  $(\text{CH}_2:\text{CMe})_2\text{SnBr}_2$ ,  $b_{10}$   $100-101^\circ$ ,  $n_D^{20}$  1.5665,  $d_{20}$  1.9363. Stirring 3 g.  $(\text{CH}_2:\text{CMe})_2\text{TlBr}$  and 6 g.  $\text{SnBr}_2$  in 50 ml.  $\text{Me}_2\text{CO}$  5 hrs. at room temp. and 3 hrs. at  $50^\circ$  gave a ppt. which was sepd. Concn. of the filtrate gave 0.38 g. original  $(\text{CH}_2:\text{CMe})_2\text{TlBr}$ . The residual liquid, after concn., was extd. with petr. ether and the ext. treated with 20% KOH, the resulting solid being treated with 15% HBr; this treatment yielded an unstated amount of  $(\text{CH}_2:\text{CMe})_2\text{SnBr}_2$ ,  $b_9$   $102.5^\circ$ ,  $n_D^{20}$  1.5664. The original ppt. was identified as TlBr (73%). Stirring 3 g.  $(\text{MeCH}:\text{CH})_2\text{TlBr}$  and 6 g.  $\text{SnBr}_2$  in  $\text{C}_6\text{H}_6$  6 hrs. at  $50^\circ$  gave among undescribed products, some 1.1 g.  $(\text{MeCH}:\text{CH})_2\text{SnBr}_2$ ,  $b_{10}$   $121-22^\circ$ ,  $n_D^{20}$  1.5663. To 1 g.  $(\text{CH}_2:\text{CMe})_2\text{SnBr}_2$  in 5 ml. EtOH was added 2 g.  $\text{HgBr}_2$  in 5 ml. EtOH and 10 ml.  $\text{H}_2\text{O}$ ; after brief heating and addn. of 15 ml.  $\text{H}_2\text{O}$ , followed by 12 hrs. standing, there was obtained 43%  $(\text{CH}_2:\text{CMe})\text{HgBr}$ , m.  $167^\circ$  (from  $\text{Me}_2\text{CO}$ ). To 1 g.  $(\text{CH}_2:\text{CMe})_2\text{SnBr}_2$  in 10 ml. MeOH was added 15 ml. 20% NaOH which dissolved the originally formed solid; the mixture was treated with 1 g.  $\text{HgBr}_2$  in 10 ml. MeOH and kept 2 hrs. after which it was extd. with  $\text{Et}_2\text{O}$ , the ext. yielding 79% liquid  $(\text{CH}_2:\text{CMe})_2\text{Hg}$ , which with  $\text{HgBr}_2$  in  $\text{Me}_2\text{CO}$  gave  $\text{CH}_2:\text{CMeHgBr}$ , m.  $166-67^\circ$ . To 1 g.  $(\text{CH}_2:\text{CMe})_2\text{Hg}$  in  $\text{Et}_2\text{O}$  was added 0.8 g.  $\text{TlBr}_3$  in  $\text{Et}_2\text{O}$ ; after 1 hr. the thickened mixt. was treated with 20 ml.  $\text{C}_6\text{H}_6$ , warmed on a steam bath and filtered; this gave 89%  $(\text{CH}_2:\text{CMe})_2\text{TlBr}$ , dec.  $190-94^\circ$ , while the evapd. filtrate gave 70%  $\text{CH}_2:\text{CMeHgBr}$ , m.  $167^\circ$ . Stirring 5.9 g.  $(\text{CH}_2:\text{CMe})_2\text{Hg}$  and 12 g.  $\text{SnBr}_2$  in petr. ether 5 hrs. and washing the sepd. ppt. with petr. ether and  $\text{Me}_2\text{CO}$  gave on evapn. of the  $\text{Me}_2\text{CO}$  soln. 1.72 g.  $\text{CH}_2:\text{CMeHgBr}$ ; the petr. ether soln. gave a liquid which treated with 20% KOH and the resulting solid treated with 15% HBr, gave some  $(\text{CH}_2$

some  $(\text{CH}_2:\text{CMe})_2\text{SnBr}_2$  while the alkaline soln. on extn. with  $\text{Et}_2\text{O}$  gave 0.6 g.  $(\text{CH}_2:\text{CMe})_4\text{Sn}$ ,  $b_8$  66-67°,  $n_D^{20}$  1.5110,  $d_{20}$  1.3153; and 44% Hg was also isolated. Reaction of 4 g.  $(\text{CH}_2:\text{CMe})_2\text{Hg}$  with 8 g.  $\text{SnBr}_2$  in 20 ml. petr. ether 5 hrs. at 65° gave 1.03 g.  $\text{CH}_2:\text{CMeHgBr}$ , 1.1 g.  $(\text{CH}_2:\text{CMe})_2\text{SnBr}_2$ , 0.4 g.  $(\text{CH}_2:\text{CMe})_4\text{Sn}$  and 2.05 g. Hg. To 1 g.  $(\text{CH}_2:\text{CMe})_2\text{Hg}$  in 5 ml.  $\text{Me}_2\text{CO}$  was added 2 g.  $\text{SnBr}_2$  in 10 ml.  $\text{Me}_2\text{CO}$  yielding a ppt. of Hg immediately; after 20 hrs. at room temp. there was isolated: 0.57 g.  $\text{CH}_2:\text{CMeHgBr}$ , 0.22 g.  $(\text{CH}_2:\text{CMe})_2\text{SnBr}_2$ , 0.2 g.  $(\text{CH}_2:\text{CMe})_4\text{Sn}$  and 0.32 g. Hg. To 1 g.  $(\text{CH}_2:\text{CMe})_2\text{Hg}$  was added 2 g. powd.  $\text{SnBr}_2$  (somewhat exothermic) and after 20 hrs. at room temp., the mixt. gave 0.42 g.  $\text{CH}_2:\text{CMeHgBr}$ , 0.1 g.  $(\text{CH}_2:\text{CMe})_2\text{SnBr}_2$ , 0.3 g.  $(\text{CH}_2:\text{CMe})_4\text{Sn}$  and 0.35 g. Hg.

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*Organic*

Synthesis of organo-tin compounds from organomercury compounds and salts of divalent tin in inert solvents.

A. N. Nesmeyanov, A. E. Borisov, N. V. Novikova and M. A. Osipova. (Inst. Hetero-org. Compds., Moscow). Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 263-66. Cf. J. Rus. Phys. Chem. Soc. 62, 1796 (1931).

Stirring 5.9 g.  $(\text{CH}_2:\text{CMe})_2\text{Hg}$  and 12 g.  $\text{SnBr}_2$  in 30 ml. petr. ether 5 hrs., sepg. the ppt. and washing it with petr. ether then with  $\text{Me}_2\text{CO}$  gave on evapn. of the  $\text{Me}_2\text{CO}$  soln. 1.72 g.  $\text{CH}_2:\text{CMeHgBr}$ . Evapn. of the petr. ether soln. gave a liquid which treated with 20% KOH gave a ppt. which with 15% HBr gave 22%  $(\text{CH}_2:\text{CMe})_2\text{SnBr}_2$ ,  $b_9$  102.5°,  $n_D^{20}$  1.5667,  $d_{20}$  1.9360; the alkaline soln. on extn. with  $\text{Et}_2\text{O}$  gave 0.6 g.  $(\text{CH}_2:\text{CMe})_4\text{Sn}$ ,  $b_8$  66-67°,  $n_D^{20}$  1.5110,  $d_{20}$  1.3153; the reaction also gave 1.86 g. Hg. Similar reaction run at 65° gave 71% Hg, 21%  $(\text{CH}_2:\text{CMe})_2\text{SnBr}_2$  and small amounts of  $\text{CH}_2:\text{CMeHgBr}$  and  $(\text{CH}_2:\text{CMe})_4\text{Sn}$ . Similar reaction in  $\text{Me}_2\text{CO}$  at room temp. also gave the same 4 products. Stirring 5 g.  $\text{Et}_2\text{Hg}$  and 7 g.  $\text{SnCl}_2$  in ligroin 12 hrs. at 90° followed by sepn. of the ppt. and washing it with hot petr. ether and MeOH gave, from petr. ether soln. 2.5 g.  $\text{Et}_2\text{SnCl}_2$ , m. 83-3.5°, while the MeOH

soln. gave ~~2.59 g.~~ 1 g.  $\text{EtHgCl}$ ; 2.59 g. Hg was isolated. Powd.  $\text{Ph}_2\text{Hg}$  (3 g.) and 3 g.  $\text{SnCl}_2$  in ligroin in 7 hrs. at  $60-65^\circ$  gave 1.66 g. Hg and 75%  $\text{Ph}_3\text{SnCl}$ , m.  $102-104^\circ$  (from petr. ether). Similarly 2 g.  $\text{Ph}_2\text{Hg}$  and 2 g.  $\text{SnBr}_2$  in ligroin gave in 12 hrs. at  $60-70^\circ$  0.27 g.  $\text{Ph}_3\text{SnCl}$ , 0.33 g.  $\text{PhHgBr}$  and 1.5 g. Hg. Similarly 3 g.  $(p\text{-MeC}_6\text{H}_4)_2\text{Hg}$  and 3 g.  $\text{SnCl}_2$  in ligroin in 13 hrs. at  $90-5^\circ$  gave after the above described treatment, 72%  $(p\text{-MeC}_6\text{H}_4)_2\text{SnCl}_2$ , m.  $49.5^\circ$  (from petr. ether) and 1.51 g. Hg. Similarly  $\text{SnCl}_2$  and  $(o\text{-MeC}_6\text{H}_4)_2\text{Hg}$  gave 66%  $(o\text{-MeC}_6\text{H}_4)_2\text{SnCl}_2$ , m.  $49.5-50^\circ$  and 100% Hg. Similarly 3.8 g.  $(1\text{-C}_{10}\text{H}_7)_2\text{Hg}$  and 4 g.  $\text{SnCl}_2$  in 20 hrs. at  $90-5^\circ$  gave 53%  $(1\text{-C}_{10}\text{H}_7)_2\text{SnCl}_2$ , m.  $130-32^\circ$  (crude), m.  $136-37^\circ$  (from petr. ether), and 95% Hg.

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*Organic*

Fluorinated styrenes. 3. Styrenes, fluorinated in the side chain.

M. M. Nad, T. V. Talalaeva, G. V. Kazernikova and K. A. Kocheshkov. *Iz* (L. Ya. Karpov Phys. Chem. Inst., Moscow). *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* 1959, 272-77. Cf. Cohen et al. *JACS* 71, 3439 (1949) and Prober *JACS* 75, 963(1953). No ref. given to parts 1 and 2.

A convenient low temp. organolithium route was developed for the synthesis of fluoroacetophenones. Under  $N_2$  atm. 240 ml. 1.42 N  $Et_2O$  soln. of  $PhLi$  was cooled to  $-72^\circ$  and treated dropwise with 11.2 g.  $CHF_2CO_2H$  in 30 ml.  $Et_2O$  over 35 min.; after stirring 2 hrs. at  $-75^\circ$ , the mixture was poured on ice-HCl and extd. with  $Et_2O$ , yielding 87%  $CHF_2COPh$ ,  $b_{26}$   $83.5-84^\circ$ ,  $n_D^{20}$  1.4984. Heating 95 g.  $KF$  in 250 ml. dry glycerol at  $170-75^\circ$  at 16-17 mm with gradual application of vacuum was then followed by addn. of  $CHCl_2COPh$  (94 g.) ~~maximized~~ over 4 hrs. at  $153-63^\circ$ ; distn. began after 40-50 min. and after gradual heating to  $190^\circ$  at 6-8 mm. there was obtained 32-6%  $CHF_2COPh$ . The ketone (31.2 g.) in 1 vol.  $MeOH$  was added over 15 min. to a soln. of 3.8 g.  $NaBH_4$  in 25 ml.  $H_2O$  and 4 ml. 2N  $NaOH$  at  $10^\circ$  initially,  $20-30^\circ$  during the bulk of the addn.; after 1 hr. stirring, the mixt. was poured into 10%  $NaOH$  and extd. with  $Et_2O$ , yielding 92.4%  $CHF_2CH(OH)Ph$ ,  $b_{20}$   $105^\circ$ ,  $n_D^{20}$  1.4940. This with  $SOCl_2$ -pyridine at below  $35^\circ$ , then at  $85-90^\circ$  0.5 hr., gave 82-86%  $CHF_2CHClPh$ ,  $b_{25}$   $89-90^\circ$ ,  $n_D^{20}$  1.4950. This, 41.1 g., mixed with 0.3 g. powd.  $Cu$ , 60 g.  $AcNH_2$  and 22.8 g.  $Zn$  dust was heated gradually to  $150^\circ$  and kept 2 hrs. at  $150-54^\circ$ , then treated with dil.  $H_2SO_4$  and extd. with  $Et_2O$ , yielding 60-65%  $PhCH:CHF$ ,  $b_{50}$   $75-6.5^\circ$ ,  $n_D^{20}$  1.5257. Similarly,  $PhLi$  and  $CF_2ClCO_2H$  gave 50%  $PhCOCClF_2$ ,  $b_{35}$   $94-96^\circ$ , 1.4950, which reduced with  $NaBH_4$  to 90-5%  $PhCH(OH)CClF_2$ ,  $b_5$   $85-6^\circ$ ; the result was the same in the reduction with  $(iso-PrO)_3Al$ - $iso-PrOH$ . The carbinol was converted as above to  $PhCHClCClF_2$ , 78%,  $b_{22.5}$   $91.5-93^\circ$ , which as above gave 60-77%  $PhCH:CF_2$ ,  $b_{62}$   $65-66^\circ$ , 1.4927; this gives a dibromide, which with  $Zn$  dust in  $AcNH_2$  again gave the original  $PhCH:CF_2$ .  $PCl_5$  and  $PhCOCHF_2$  gave 85%  $PhCCl_2CHF_2$ ,  $b_{30}$   $105.5-107^\circ$ ,  $n_D^{30}$  1.5045,  $n_D^{20}$  1.5086. This with  $SbF_3$  gave 35-40%  $PhCClFCHF_2$ ,  $b_{55}$   $92-94^\circ$ .

$n_D^{20}$  1.4683. This with Zn-Cu-AcNH<sub>2</sub> as above at 125-30° gave 43% PhCF:CHCl,  $b_{60}$  88-90°, 1.5060. Heating 128 g. PhCOCHCl<sub>2</sub> with 176 g. PCl<sub>5</sub> 0.5 hr. at 145° and 8 hrs. at 175° gave 37% PhCCl<sub>2</sub>CHCl<sub>2</sub>,  $b_3$  120-22°, which (81 g.) was heated with 45.5 g. SbF<sub>3</sub> and 1 ml. Br<sub>2</sub> under 10-11 mm. with slow distn. of products, yielding 46% PhCF<sub>2</sub>CHCl<sub>2</sub>,  $b_{10}$  84°, 1.5000, which heated as above with Zn-Cu-AcNH<sub>2</sub> at 150° 2 hrs. gave 81% PhCF:CHCl,  $b_{14}$  86-87°, 1.5531.

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### *Organic*

Reaction of -chloromethylethoxysilanes with amines.

K. A. Andrianov and L.M.Volkova (Inst. Hetero-org. Compds., Moscow). Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 277-82.

It was shown that amines react at 20° with silanes contg. the CH<sub>2</sub>Cl group and EtO groups, the rates being dependent on the amine. The following series of descending reactivity was established on the basis of kinetic curves which are shown: HOCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, Me<sub>3</sub>SiOCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, EtNH<sub>2</sub>, Et<sub>2</sub>NH, PhNH<sub>2</sub>, EtPhNH, and: ClCH<sub>2</sub>SiMe<sub>2</sub>OEt, ClCH<sub>2</sub>SiMe(OEt)<sub>2</sub>, ClCH<sub>2</sub>Si(OEt)<sub>3</sub>. Keeping 35 g. ClCH<sub>2</sub>SiMe<sub>2</sub>OEt with 50 g. EtNH<sub>2</sub> 15 days at 20° gave 65% EtNHCH<sub>2</sub>SiMe<sub>2</sub>OEt,  $b_{751}$  163.5-54.5°,  $n_D^{20}$  1.4149,  $d_{20}$  0.8358. Similarly ClCH<sub>2</sub>SiMe(OEt)<sub>2</sub> gave 56% EtNHCH<sub>2</sub>SiMe(OEt)<sub>2</sub>,  $b_{757}$  180-81°, 1.4120, 0.8870. Keeping 18.2 g. ClCH<sub>2</sub>SiMe(OEt)<sub>2</sub> and 37 g. PhNH<sub>2</sub> in 18 g. abs. EtOH 15 days gave 13.5% PhNHCH<sub>2</sub>SiMe(OEt)<sub>2</sub>,  $b_5$  125-30°, 1.4990, 1.010. The kinetic curves which are shown were obtained by reactions run at 20° with the appropriate silanes, amines and EtOH, the latter being used to dissolve the resulting amine salts.

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New methods of synthesis of organosiloxanes. *Organic*

N. F. Orlov and B. N. Dolgov (Silicate Chem. Inst., Leningrad). Doklady Akad. Nauk S.S.S.R. 125, 817-20 (1959).

Heating 10.2 g.  $\text{MeEt}_2\text{SiH}$  and 18 g.  $\text{Ph}_3\text{SiOH}$  in  $\text{C}_6\text{H}_6$  with 0.001 g. colloidal Ni 7 hrs. gave 1.5 l.  $\text{H}_2$  and 86%  $\text{MeEt}_2\text{SiOSiPh}_3$ ,  $b_5$   $212^\circ$ ,  $d_{20}$  1.0304,  $n_D^{20}$  1.5580. Similarly was prepd. 72%  $\text{MeEt}_2\text{SiOSiEt}_3$ ,  $b_{763}$   $208-9^\circ$ , 0.8323, 1.4240; 74.3%  $\text{Et}_3\text{SiOSiPh}_3$ ,  $b_2$   $205^\circ$ , 1.0275, 1.5581; 80%  $\text{MePr}_2\text{SiOSiPh}_3$ ,  $b_{3.5}$   $207^\circ$ , 1.0123, 1.5500; 78.3%  $\text{EtPr}_2\text{SiOSiPh}_3$ ,  $b_{2.5}$   $208^\circ$ , 1.0118, 1.5490. Similar use of  $\text{Ph}_2\text{Si}(\text{OH})_2$  with appropriate silanes gave: 48%  $(\text{MeEt}_2\text{SiO})_2\text{SiPh}_2$ ,  $b_3$   $185^\circ$ , 0.9704, 1.4930; 73%  $(\text{MePr}_2\text{SiO})_2\text{SiPh}_2$ ,  $b_{2.5}$   $190^\circ$ , 0.9762, 1.5024; 76%  $(\text{Et}_3\text{SiO})_2\text{SiPh}_2$ ,  $b_3$   $194^\circ$ , 0.9768, 1.5012. Also listed are:  $(\text{Et}_3\text{SiOSiEt}_2)_2\text{O}$ , 71.2%,  $b_4$   $172^\circ$ , 0.9064, 1.4390;  $\text{MePr}_2\text{SiOSiPr}_2\text{Me}$ , 74%,  $b_4$   $99^\circ$ , 0.8249, 1.4285;  $(\text{MePh}_2\text{Si})_2\text{O}$ , 83%, m.  $49^\circ$ ,  $b_6$   $203^\circ$ ;  $(\text{MeEt}_2\text{Si})_2\text{O}$ ,  $b_{760}$   $192^\circ$ , 0.8212, 1.4185, and  $(\text{Et}_3\text{Si})_2\text{O}$ ,  $b_{760}$   $233^\circ$ , 0.8457, 1.4330. Heating 20 g.  $\text{MePh}_2\text{SiH}$  with 0.02 g. ~~colloidal~~  $\text{NiCl}_2$  10 min. until colloidal Ni formed, followed by cooling, addn. of 30 ml.  $\text{MePh}$  and 1.8 ml.  $\text{H}_2\text{O}$  and heating again 4 hrs. gave 2.3 l.  $\text{H}_2$  and 83%  $(\text{MePh}_2\text{Si})_2\text{O}$ . The condensation described above evidently occurs through reaction of the silane with  $\text{H}_2\text{O}$  formed by dehydration of the silanols.

G.M. Kosolapoff,

*Organic*

Individual hydrocarbons of cyclohexane series from gasoline fractions of Sakhalin petroleum.

N. B. Podkletnov (Sakhalin Res.Inst., Acad.Sci.). Doklady Akad. Nauk S.S.S.R. 125, 821-2 (1959).

Examn. of Sakhaline petroleum gasoline fractions shows the presence of the following cyclohexane derivs.: methylcyclohexane, cyclohexane, ethylcyclohexane, 1,2- and 1,3-dimethylcyclohexanes, these groups accounting for 64-74% of the total fractions. Also found in smaller amounts were 1,4-dimethylcyclohexane, propyl- and isopropylcyclohexanes, 1,2-, 1,3-, and 1,4-methylethylcyclohexanes, 1,2,3-, 1,2,4- and 1,3,5-trimethylcyclohexanes, perhydroindane.

G.M. Kosolapoff.

Organic

**Synthesis of polymerizable methacrylates of trialkyl(aryl)tin.**

M. M. Koten, T. M. Kiseleva and V. A. Paribok (High Polymer Inst., Leningrad). Doklady Akad. Nauk S.S.S.R. 125, 1263-4 (1959).

The conventional conversion of  $R_4Sn$  to  $R_3SnCl$  and to  $R_3SnOH$  gave:  $Me_3SnOH$ , needles;  $Et_3SnOH$ ,  $b_{20}$  153-5°, m. 45°; and  $Bu_3SnOH$ ,  $b_5$  186-90°, as well as  $Ph_3SnOH$ , m. 119°. These and equimolar amt. of  $CH_2:CHCO_2H$  were heated 0.5-1.0 hr. in  $Me_2CO$  and distd., yielding 60-80% corresponding methacrylates:  $Me_3SnO_2CCMe:CH_2$ , m. 122°; tri-Et analog, m. 76-9°; tri-Bu analog, m. 20-2°; tri-Ph analog, m. 91-2° (with alc. HCl this gave the free acid and  $Ph_3SnCl$ ). Alc. KOH gave  $CH_2:CHCO_2K$  and  $Ph_3SnOH$ . The esters polymerize both in the absence of added catalysts and with peroxides and azo compds.

G.M. Kosolapoff.



*Organic***Polymerization of vinylaromatic organosilicon compounds. Derivatives of  $\alpha$ -methylstyrene.**

V. V. Kershak, A. M. Polyakova, A. A. Sakharova, A. D. Petrov and E. A. Chernyshev (Inst. Hetero-org. Compds., Moscow). Doklady Akad. Nauk S.S.S.R. 126, 791-3 (1959).

Polymerization of  $R_3SiC_6H_4CMe:CH_2-p$  was run either with  $(Me_2C(CN)N:)_2$  at  $80^\circ$  or  $(Me_3CO)_2$  at  $130^\circ$  under 600 atm. ( no polymerization occurred without pressure ) 6 hrs. and glassy polymers were obtained from monomers with ~~at~~ p-substituents of:  $Et_3Si$ ,  $Et_3SiCH_2$ ,  $Et_3SiCH_2CH_2$ , and  $Me_3SiCH_2$ . The nitrile was the more effective catalyst. Characteristic viscosities and thermomechanical<sup>1</sup> properties of the polymers are shown graphically. In general, viscosities decrease in passing from  $PhCMe:CH_2$  to  $Et_3SiC_6H_4CMe:CH_2$  and to the more complex polymers. For synthesis of the monomers see Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, no pp. given (Petrov, Chernyshev and Tolstyakova).

G.M. Kosolapoff.

*Organic***Addition reaction of trialkoxysilanes to olefins.**

N. S. Nametkin, A. V. Topchiev, T. I. Chernysheva and L. I. Kartasheva (Petrochem. Synth. Inst., Moscow). Doklady Akad. Nauk S.S.S.R. 126, 794-7 (1959). cf. US Pat. 2,637,737; C.A. 8254 (1954).

Addn. of 24.6 g.  $(EtO)_3SiH$  to 18.9 g. 1-nonene and 1 ml. chloroplatinic acid soln. at  $100-10^\circ$  and heating 2-3 hrs. gave 41.4%  $C_9H_{19}Si(OEt)_3$ ,  $b_2$   $130-3^\circ$ ,  $n_D^{20}$  1.4182,  $d_{20}$  0.8827. Similarly were obtained: 18.2%  $C_8H_{17}Si(OCMe_3)_3$ ,  $b_2$   $138-40^\circ$ , 1.4200, 0.8650;  $C_8H_{17}Si(OBu)_3$ , 21.1%,  $b_2$   $155-8^\circ$ , 1.4280, 0.8747; 64.9%  $C_9H_{19}Si(OCHMe_2)_3$ ,  $b_2$   $128-32^\circ$ , 1.4180, 0.8589; 43.1%  $C_9H_{19}Si(OBu)_3$ ,  $b_2$   $164-6^\circ$ , 1.4298, 0.8715; 37.8%  $C_9H_{19}Si(OCHEt)_3$ ,  $b_2$   $160-4^\circ$ , 1.4270, 0.8714; 12.5%  $C_9H_{19}Si(OCMe_3)_3$ ,  $b_2$   $150-5^\circ$ , 1.4232, 0.8622; 78.4%  $C_9H_{19}Si(OCH_2CHMe_2)_3$ ,  $b_4$   $175-6^\circ$ , 1.4260, 0.8700; 65.2%  $C_{10}H_{21}Si(OBu)_3$ ,  $b_2$   $167-70^\circ$ , 1.4315, 0.8710; and 20.5%  $C_{10}H_{21}Si(OCMe_3)_3$ ,  $b_2$   $160-1^\circ$ , 1.4260, 0.8589. The addn. occurs contrary to Markovnikov rule.

G.M. Kosolapoff.

*Organic*

**Synthesis of triethylsiloxy derivatives of vanadium and antimony.**

K. A. Andrianov, A. A. Zhdanov and E. A. Kashutina (Inst. Hetero-org. Compds., Moscow). Doklady Akad. Nauk S.S.S.R. 126, 1261-3 (1959).

To 37.5 g.  $\text{Et}_3\text{SiONa}$  in 200 ml.  $\text{C}_6\text{H}_6$  was added dropwise 14 g.  $\text{VOCl}_3$  in 50 ml.  $\text{C}_6\text{H}_6$  over 40 min.; after filtration there was obtained 60% pale yellow  $(\text{Et}_3\text{SiO})_3\text{VO}$ ,  $b_{3.5}$  186.5°,  $d_{20}$  0.9816,  $n_D^{20}$  1.4820. Similarly  $\text{SbCl}_3$  gave 56%  $(\text{Et}_3\text{SiO})_3\text{Sb}$ ,  $b_{1.5}$  160-2°, 1.1037, 1.4681. To 58 g.  $[\text{2Pb}(\text{OSiEt}_3)_2 \cdot \text{Pb}(\text{OH})_2]$  in 100 ml.  $\text{C}_6\text{H}_6$  was added 14.4 g.  $\text{TiCl}_4$  in  $\text{C}_6\text{H}_6$  over 1.5 hrs. and the filtered soln. gave 50%  $(\text{Et}_3\text{SiO})_4\text{Ti}$ ,  $b_{2.5}$  176-8°, m. 96°. The use of  $\text{VOCl}_3$  similarly gave  $(\text{Et}_3\text{SiO})_3\text{VO}$ ,  $b_{1.5}$  169-71°, 0.9809, 1.4812. Infrared spectra of the products are reported.

G.M. Kosolapoff.

*Organic*

**Catalytic hydrogenation of diene hydrocarbons with a system of isolated double bonds in the presence of platinum and palladium.**

S. A. Kazanskii, I. V. Gestunskaya and A. I. Leonova (M. V. Lomonosov State Univ., Moscow). Doklady Akad. Nauk S.S.S.R. 126, 1264-7 (1959).

Hydrogenation of 1,5-hexadiene over  $\text{Pt}$  black at room temp. in 95%  $\text{EtOH}$  gave after the uptake of 0.5 mole  $\text{H}_2$  27% 1-hexene, 12% hexane and 61% unreacted diene. Similar reaction over  $\text{Pd}$  black gave 23% 1-hexene, 27% 2-hexene, 33% unreacted diene and 17% 1,4-hexadiene. 2-Methyl-1,5-hexadiene over  $\text{Pd}$  black gave ~~mainly~~<sup>no</sup> 2-methyl-2,4-hexadiene and the reaction mixt. was too complex to be analyzed. 2-Methyl-2,5-hexadiene over  $\text{Pd}$  gave some 15% 2-methyl-2,4-hexadiene and a mixt. of unidentified products. 2,5-Dimethyl-1,5-hexadiene over  $\text{Pd}$  black gave some 2,5-dimethyl-1,4-hexadiene and unidentified other products.

G.M. Kosolapoff.

*Organic*

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Ferrocenylboronic and 1,1'-ferrocenyldiboronic acids and their reactions.

A. N. Nesmeyanov, V. A. Sazonova and V. N. Drozd (M. V. Lomonosov State Univ., Moscow). Doklady Akad. Nauk S.S.S.R. 126, 1004-6 (1959).

The reactions were run under  $H_2$ . To 92 g.  $(BuO)_3B$  in  $Et_2O$  there was added with Dry Ice Cooling an ethereal soln. of ferrocenyl-lithium prepd. from 17.6 g. ferrocene by treatment with  $BuLi$  (from 39 g.  $BuCl$  and 7.6 g.  $Li$ ); the mixt. was allowed to come to room temp. and on the following day was treated with aq.  $H_2SO_4$ , and the org. layer was extd. with aq.  $KOH$ ; the alkaline exts. on acidification gave first 2.9 g. 1,1'-ferrocenylenediboronic acid (total 13%), dec.  $180^\circ$  (from  $H_2O$ ), then ferrocenylboronic acid, 26%, m.  $143-8^\circ$  (from  $H_2O$ ). The latter refluxed with aq.  $ZnCl_2$  gave ferrocene; the diboronic acid is hydrolyzed similarly. Treatment of I with hot aq. acetone soln. of  $HgCl_2$  gave 76% yellow ferrocenylmercuric chloride, dec.  $192-4^\circ$  (from xylene). Similarly aq.  $CuCl_2$  gave 84% chloroferrocene, m.  $59-60^\circ$  (from  $EtOH$ ).  $CuBr_2$  gave 80% bromoferrocene, m.  $32-3^\circ$ . A and hot aq.  $CuCl_2$  gave 1,1'-dichloroferrocene, m.  $75-7^\circ$  (from  $EtOH$ );  $CuBr_2$  gave 76% 1,1'-dibromoferrocene, m.  $50-1^\circ$  (from  $EtOH$ ). Treatment of I with ammoniacal soln. of  $Ag_2O$  gave metallic  $Ag$  and extr. with  $Et_2O$  gave 52% diferrocenyl, dec.  $230^\circ$ , along with 31% ferrocene. Diferrocenyl is sparingly sol. in petr. ether, sol. in  $MePh$ ,  $C_6H_6$ , dioxane and tetrahydrofuran.

G.M. Kosolapoff.

#### Diferrocenyl.

*Organic*

O. A. Nesmeyanova and E. G. Perevalova (M. V. Lomonosov State Univ., Moscow). Doklady Akad. Nauk S.S.S.R. 126, 1007-8 (1959).

Heating diferrocenylmercury with  $Pd$  black gave at best 6.2% diferrocenyl, with ferrocene being the main product (up to 49%). This can be explained by disproportionation of ferrocenyl free radicals formed initially. The products were sep'd. chromatographically on  $Al_2O_3$ , ferrocene being eluted with petr. ether, diferrocene with petr. ether- $C_6H_6$ . The residues contained some ferrocene polymers. Diferrocenyl is orange, dec.  $230^\circ$ ; thermal decompn. does not yield ferrocene.

G.M. Kosolapoff.

Boron compounds. Reactivity of triallylboron. *Organic*

A. V. Topchiev, Ya. M. Faushkin, A. A. Prokhorova and M. V. Kurashev.  
Doklady Akad. Nauk S.S.S.R. 128, 110-12 (1959).

All expts. listed below were run under  $N_2$ . Reaction of 60 g.  $CH_2:CHCH_2Br$ , 48 g. Mg and 37 g.  $BF_3 \cdot Et_2O$  in 500 ml.  $Et_2O$  gave up to 92%  $(CH_2:CHCH_2)_3B$ ,  $b_{15} 62-5^\circ$ ,  $d_{20} 0.7178$ , (I). Addn. of 3.55 g. AcOH to 7.88 g. I gave propylene and 46.9%  $(CH_2:CHCH_2)BOAc$ , b.  $138-40^\circ$ . I (3.81 g.) and 2.61 g. abs. EtOH gave 52%  $CH_2:CHCH_2B(OEt)_2$ ,  $b_{10} 43-6^\circ$ .  $CH_2:CHCH_2OH$  and I gave  $C_3H_6$  and  $CH_2:CHCH_2B(OCH_2CH:CH_2)_2$ ,  $b_6 50-1^\circ$ . Reaction of 8.8 g. I and 3 g. AcH gave 56.4%  $(CH_2:CHCH_2)_2BOEt$ ,  $b_7 48-9^\circ$ . Reaction of 0.6 g. I and 2.1 g.  $Br_2$  in  $CCl_4$  gave undistillable  $(Br_2C_3H_5)_3B$ , the addn. to the last allyl group requiring some 30 days at room temp. Mixing 1.25 g. pyridine and 2.1 g. I gave an exothermic reaction and a subsequent distn. gave  $(C_3H_5)_3B \cdot C_5H_5N$ ,  $b_4 116-8^\circ$ .

G.M. Kosolapoff.

Intermediate stages of synthesis of tetracyclines. *Organic*

M. M. Shemyakin, M. N. Kolosov, Yu. A. Arbuzov, Se Yui Yuan, Shen Khuai Yui, K. A. Sklobovskii, M. G. Karapetyan and A. I. Gurevich (M. D. Zelinskii Inst. Org. Chem., Moscow). Doklady Akad. Nauk S.S.S.R. 128, 113-6 (1959).  
cf. this j. 112, 669 (1957).

Bromination of compds. of type I ( $R-R'-H$ ;  $R-H$ ,  $R'-Ac$ ;  $R-OMe$ ,  $R'-H$ ;  $R-OMe$ ,  $R'-Ac$ ) in  $CHCl_3$  at  $-60^\circ$  gave 60-70% corresponding dibromides II (m.  $146^\circ$ , m.  $174^\circ$ , -, -). Oxidation of I with  $BzO_2H$  in  $CHCl_3$  at  $20^\circ$  gave 85-95% corresponding epoxides III (m.  $138^\circ$ ; m.  $189^\circ$ , m.  $211^\circ$ , resp.). Both reactions are stereospecific and yield products with the electrophilic group in the position 3. The same rule applies to addn. of  $HOCl$  or  $HOBr$  to I in the reaction of  $Me_3COCl$  in aq.  $Me_2CO$  at  $20^\circ$  or  $(CH_2CO)_2NBr$  in 0.01N aq.  $Me_2CO$  soln. of  $H_2SO_4$  at  $0^\circ$ ; the 1st of these reactions yields chlorohydrins IV in 75-85% yields (m.  $211^\circ$ ; m.  $158^\circ$ ; m.  $210^\circ$ , resp.); the 2nd reaction gave the mixed isomeric bromohydrins V and VI in 1:2 ratio, with the addn. taken

place in all cases in positions 2, 3. Chlorohydrins or bromohydrins V can be also prepd. by ring opening in III by means of pyridine.HBr or pyridine.HCl in refluxing EtOH. The reverse reaction of ring closure is readily attained with KOH in 70% dioxane. The isomeric halohydrins IV yield the stereoisomeric epoxides VII (m. 141°; m. 191°; m. 174°, resp.). Addn. of HOCl to IX (R-H, or R-MeO) or chlorination in CHCl<sub>3</sub> at ~~max~~<sup>0</sup> -50° gave after an aq. treatment with CaCO<sub>3</sub> unstable chloroketones X (m. 211°; m. 158°; m. 210°, resp.), while XI (R-H or MeO) similarly gave XII (R-R'-R''=H, X=Cl; R-R''=H, X=Cl; R-R'-H, R-MeO, X=Cl; m. 88°; m. 119°; m. 121°, resp.); the analogous bromoketones (m. 64°, m. 57°; m. 70°, and m. 68°, and m. 66°, resp.) are also obtained in 75-90% yields by oxidation of the halohydrins with CrO<sub>3</sub> in 80% AcOH. These halo ketones are dehalogenated with Zn dust in AcOH at 30° to the hydroxy ketones X(R-R'-H, X-H, m. 121°; R-OMe, R'-H, X-H, m. 192°) or XII (R-R'-R''=H, X-H, m. 135°, and R-R'-H, R''-OMe, X-H, m. 161°), also obtained by hydrolysis of IX with dil. HCl in 70% EtOH at 40°. Reaction of Me<sub>3</sub>COK and III(R-R'-H) gave XIII (~~X=H, Y'-OH, X'-Y'-O~~) (m. 135°) which was oxidized to the corresponding diketo-epoxide, m. 152°. Similarly XIV (Z=O) (m. 162°) gave the 3,9-oxide XIII(X-H, Y'-OH, X'=H, Y'=OH; m. 176°), through reduction of appropriate I with LiAlH<sub>4</sub> to the glycol XIV(m. 204°) and its oxidation with BzO<sub>2</sub>H. All compds. shown in this paper have the structure of 4a H, 9 OH, 9a H with the cis-conformation of the B and C rings being most stable. Condensation of II with NaHC(CO<sub>2</sub>Et)<sub>2</sub> in the presence of 2EtONa and hydrolysis <sup>unsatd. malonate</sup> gave ~~the~~ XV (m. 127°, ~~monohydrate~~) ~~which is a dioxane derivative~~. Similar condensation of X(R-R'-H, X=Cl, m. 88°) gave 2,9-epoxyketone, m. 160°, and the oxomalonate, isolated as bis-p-nitrophenylhydrazone, m. 272°. Thus, introduction of functional groups in ring B opens the synthesis of ring A.

*Organic*  
A new method of synthesis of organosilicon aromatic monomers.

B. A. Chernyshev, Li Guan Lian and A. D. Petrov (N. D. Zelinskii Inst. Org. Chem., Moscow). Doklady Akad. Nauk S.S.S.R. 127, 808-11(1959). cf. Invest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1958, No.8 no pp given.

Passage of  $ArX$  with a  $Si-H$  bearing compd. through an empty quartz tube at  $550-700^{\circ}$  yields arylchlorosilanes. Thus  $PhCl$  and  $Cl_3SiH$  gave up to 50%  $PhSiCl_3$ , along with  $SiCl_4$  and  $C_6H_6$ . The best yield is obtained at nearly  $700^{\circ}$  with contact time of 15.7 sec. or at  $620^{\circ}$  with 70 sec. contact. The best ratio of  $PhCl$  to  $HSiCl_3$  is 2:1. Under such conditions  $PhCl$  and  $MeSiHCl_2$  gave up to 35%  $MePhSiCl_2$ , best at  $640^{\circ}$ . At  $640^{\circ}$   $1-C_{10}H_7Cl$  and  $p-Cl_2C_6H_4$  gave resp. 60%  $C_{10}H_7SiCl_3$  or 50%  $C_{10}H_7SiMeCl_2$ , or 30%  $ClC_6H_4SiCl_3$  and 20%  $ClC_6H_4SiMeCl_2$ , resp. Any packing in the tube reduces the yields.

G.M. Keselapoff.

### Synthesis of polymers with alternating siloxane and hydrocarbon links.

A. D. Petrov and V. M. Vdovin (M. D. Zelinskii Inst. Org. Chem., Moscow).  
Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1959, 1140-2.

Heating 10.5 g.  $\text{Me}_2\text{Si}(\text{CH}_2\text{CH}(\text{CH}_3)_2)_2$ , 0.02 ml. 0.1N  $\text{H}_2\text{PtCl}_6$  in iso-PrOH with 3/4 ml.  $\text{MeEtSiHCl}$  to  $65^\circ$  resulted in an exothermic reaction, after which the remaining  $\text{MeEtSiHCl}$  (total 16.3 g.) was added and after 3 hrs. at  $180^\circ$  there was obtained 88%  $\text{Me}_2\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Cl})_2$ ,  $b_3$  148-50<sup>(I)</sup>,  $d_{20}$  0.9505,  $n_D^{20}$  1.4650. Similarly were prepd.: 92%  $\text{O}(\text{SiMe}_2\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Cl})_2$ ,  $b_2$  171.5-2.5<sup>(II)</sup>, 0.9616, 1.4597; 84%  $(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Cl})_2$ ,  $b_2$  109-10<sup>0</sup>, 0.9651, 1.4610; 82.5%  $(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiEt}_2\text{Cl})_2$ ,  $b_2$  132-3<sup>0</sup>, 0.9705, 1.4666; from appropriate unsatd. silanes. I and  $\text{H}_2\text{O}$ , finally at 40-50<sup>0</sup> 10 hrs., gave a ~~gummy~~ rubbery ~~polymer~~ polymer with links of  $\text{SiMe}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SiMe}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SiMe}_2\text{O}$ . II gave an oily polymer with links of  $\text{SiMeEtCH}_2\text{CH}_2\text{SiMeEtO}$ . The other chlorides gave hard, rubbery polymers on being hydrolyzed with  $\text{H}_2\text{O}$  as above.

**G. M. Kosolpoff.**

*Organic*

# Alkoxysilanes. XIII. Reaction of siloxanes with alkoxysilanes. New method of synthesis of alkoxysilanes and siloxanes.

M. G. Voronkov (Silicate Chem. Inst., Leningrad). Zhur. Obsheei Khim. 29, 907-15 (1959). cf. 28,2128(1958).

The following starting materials were used to study exchange reactions of alkoxysilanes and siloxanes:  $(\text{MeO})_4\text{Si}$ , m.  $4.5^\circ$ ,  $b_{760}$   $121^\circ$ ,  $d_{20}$  1.035,  $n_D^{20}$  1.3689;  $(\text{EtO})_4\text{Si}$ ,  $b_{760}$   $168.3^\circ$ , 0.93343, 1.3830;  $(\text{PrO})_4\text{Si}$ ,  $b_{10}$   $107^\circ$ , 0.9112, 1.4012;  $(\text{iso-PrO})_4\text{Si}$ ,  $b_{760}$   $185.5^\circ$ , 0.8751, 1.3851;  $(\text{BuO})_4\text{Si}$ ,  $b_{10}$   $150^\circ$ , 0.89-82, 1.4134;  $(\text{iso-BuO})_4\text{Si}$ ,  $b_{10}$   $127^\circ$ , 0.8857, 1.4068;  $[(\text{MeO})_3\text{Si}]_2\text{O}$ ,  $b_1$   $58^\circ$ , 1.1222, 1.3806;  $(\text{MeO})_8\text{Si}_3\text{O}_2$ ,  $b_1$   $107^\circ$ , 1.1355, 1.3869;  $[(\text{EtO})_3\text{Si}]_2\text{O}$ ,  $b_1$   $99^\circ$ , 0.9979, 1.3915;  $(\text{EtO})_8\text{Si}_3\text{O}_2$ ,  $b_1$   $132^\circ$ , 1.0300, 1.3950;  $(\text{EtO})_{10}\text{Si}_4\text{O}_3$ ,  $b_5$   $171^\circ$ , -, 1.3978;  $[(\text{EtO})_2\text{SiO}]_4$ , m.  $8^\circ$ ,  $b_3$   $156^\circ$ , 1.0972, 1.4016;  $(\text{Me}_2\text{SiO})_3$ ,  $b_{760}$   $134.6^\circ$ , m.  $64.5^\circ$ ;  $(\text{Me}_2\text{SiO})_4$ , m.  $17.6^\circ$ ,  $b_{760}$   $175.8^\circ$ , 0.9561, 1.3968;  $(\text{Me}_2\text{SiO})_5$ ,  $b_{20}$   $101^\circ$ , 0.9597, 1.3982;  $(\text{Me}_2\text{SiO})_{2760}$ , mol.wt. 204700;  $(\text{Et}_2\text{SiO})_3$ , m.  $14^\circ$ ,  $b_{10}$   $122.5^\circ$ , 0.9555, 1.4308;  $(\text{Et}_2\text{SiO})_4$ ,  $b_{10}$   $160^\circ$ , 0.9636, 1.4358;  $(\text{Me}_3\text{Si})_2\text{O}$ ,  $b_{760}$   $100.4^\circ$ , 0.7636, 1.3774;  $(\text{Et}_3\text{Si})_2\text{O}$ ,  $b_{10}$   $103^\circ$ , 0.8443, 1.4340;  $(\text{Me}_3\text{SiO})_4\text{Si}$ ,  $b_{1.5}$   $69^\circ$ , 0.8675, 1.3892;  $(\text{Me}_3\text{SiO})_3\text{SiMe}$ ,  $b_{760}$   $190^\circ$ , 0.8500, 1.3879;  $(\text{Me}_3\text{SiO})_2\text{SiMe}_2$ ,  $b_{760}$   $152.5^\circ$ , 0.8200, 1.3849;  $(\text{BuOSiMe}_2)_2\text{O}$ ,  $b_{10}$   $100^\circ$ , -, 1.405;  $\text{Me}_3\text{SiOAm}$ ,  $b_{760}$   $145^\circ$ , -, 1.4000;  $\text{MeSi}(\text{OBu})_3$ ,  $b_{10}$   $114^\circ$ , 0.8771, 1.4109. Distn. of 29.7 g. methylsiloxane polymer (linear or cyclic) with 83.3 g.  $\text{Si}(\text{OEt})_4$  in the presence of 0.5-1.0 g. KOH gave  $\text{Me}_2\text{Si}(\text{OEt})_2$  in 80-6% yield and a solid residue of substantially  $\text{SiO}_2$ . Similarly, liq. poly-(dimethylsiloxanes) and  $(\text{iso-BuO})_4\text{Si}$  gave 93%  $\text{Me}_2\text{Si}(\text{OBu-iso})_2$ . This reaction with  $(\text{Me}_3\text{SiO})_4\text{Si}$  and  $\text{Si}(\text{OEt})_4$  gave 78%  $\text{Me}_3\text{SiOEt}$ . Numerous other examples are given for such radical exchange in the presence of KOH. This reaction of 37.1 g.  $(\text{Me}_2\text{SiO})_4$  with 208.3 g.  $(\text{EtO})_4\text{Si}$  gave 100%  $\text{Me}_2\text{Si}(\text{OEt})_2$ ; the filtered residue was heated with a little metaphosphoric acid in a dist. app., yielding 42 g.  $(\text{EtO})_4\text{Si}$  and a residue of poly-(ethoxysiloxanes),  $b_p$   $110-280^\circ$ , from which hexaethoxy and octaethoxy members were isolated. The following products are reported as a result of the above-described disproportionation reactions:  $\text{Me}_3\text{SiOMe}$ ,  $b_{760}$   $57.2^\circ$ , -, 1.3679;  $\text{Me}_3\text{SiOEt}$ ,  $b_{760}$   $75.1^\circ$ .



0.7573, 1.3742;  $\text{Me}_3\text{SiOPr}$ ,  $b_{760}$  98.5°, 0.7668, 1.3838;  $\text{Me}_2\text{Si}(\text{OMe})_2$ ,  $b_{760}$  82.2°, -, 1.3705;  $\text{Me}_2\text{Si}(\text{OEt})_2$ ,  $b_{760}$  113.8°, 0.8401, 1.3814;  $\text{Me}_2\text{Si}(\text{OPr})_2$ ,  $b_{760}$  152°, 0.8417, 1.3954;  $(\text{iso-PrO})_2\text{SiMe}_2$ ,  $b_{760}$  133°, -, 1.3863;  $\text{Me}_2\text{Si}(\text{OBu})_2$ ,  $b_{760}$  190.3°, 0.8431, 1.4058;  $(\text{iso-BuO})_2\text{SiMe}_2$ ,  $b_{760}$  172°, 0.8323, 1.3999;  $\text{Me}_2\text{Si}(\text{OAm})_2$ ,  $b_{760}$  225.5°, 0.8444, 1.4138;  $(\text{iso-BuO})_2\text{SiEt}_2$ ,  $b_{760}$  210°, 0.8455, 1.4130;  $\text{MeSi}(\text{OMe})_3$ ,  $b_{760}$  103.5°, -, 1.3701;  $\text{MeSi}(\text{OEt})_3$ ,  $b_{760}$  143.5°, 0.8949, 1.3832;  $(\text{MeO})_4\text{Si}$ ;  $(\text{EtO})_4\text{Si}$ ;  $(\text{EtO})_8\text{Si}_3\text{O}_2$ ;  $(\text{EtO})_6\text{Si}_2\text{O}$ ;  $[(\text{BuO})_2\text{SiMe}]_2\text{O}$ ;  $[(\text{BuO})_2\text{SiMeO}]_2\text{Si}(\text{OBu})\text{Me}$ ,  $b_{0.5}$  165-70°, -, 1.4155;  $(\text{Me}_3\text{Si})_2\text{O}$ . The probable scheme of the disproportionation reactions involves equilibria between the constituents of the reaction mixt. and the base catalyst ions.

Cf. Malatesta, Gaz.Ch.Ital.78,747(1948).

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*Organic*

Preparation of ketones containing a tin atom in  $\alpha$ -position relative to the carbonyl group.

A.N.Nesmeyanov, I.F.Lutsenko and S.V.Ponomarev (M.V.Lomonosov State Univ., Moscow). Doklady Akad. Nauk SSSR, 124, 1073-75 (1959). Cf. 120, 1049(1958). Mixing equimolar amounts of  $R_3SnOMe$  and an enol acetate results in an exothermic reaction which yields an alkyl acetate and an Sn-bearing ketone, the structure of the latter being confirmed by Raman and infrared spectra. Thus 11.8 g.  $Et_3SnOMe$  and 5 g.  $AcOOMe:CH_2$  gave after 0.5 hr. at  $50^\circ$  some  $MeOAc$  and 95%  $Et_3SnCH_2Ac$ ,  $b_p$   $100.5-101^\circ$ ,  $n_D^{20}$  1.4991,  $d_{20}$  1.2875, which with  $H_2O$  rapidly gave triethyltin oxide, m.  $44^\circ$ . Similarly were prepd.: 72% 2-oxocyclohexyl-triethyltin,  $b_4$   $116-17^\circ$ , 1.5057, 1.2872; 78%  $Pr_3Sn-CH_2Ac$ ,  $b_1$   $93-100^\circ$ , 1.4865, 1.1983; 85%  $Bu_3SnCH_2Ac$ ,  $b_2$   $130-32^\circ$ , 1.4842, 1.1255; and 70% 2-oxocyclohexyl-tributyltin,  $b_1$   $155-56^\circ$ , 1.4805, 1.1290. Attempts to prepare metallate  $AcM$  from  $AcOCH:CH_2$  and  $R_3SnOMe$  failed as the expected product decomposes on distn. It is pointed out that the well characterized  $Bu_3SnCH_2AC$  prepared in this work is different from the product of this alleged structure cited by Leshre et al (Bull. Soc Chim. France, No.10, 1204 (1957)).

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*Organic*

The character of cyclization of pseudoionone. A new method of preparation of  $\alpha$ -ionone.

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The cyclization of pseudoionone under the influence of 100%  $H_2SO_4$  was studied over the temp. range  $60^\circ$  to  $-60^\circ$ . To 15 ml.  $H_2SO_4$  was added 10 g. pseudoionone dissolved in 20 ml.  $MeNO_2$  with stirring and the mixture was stirred 3-300 min. after which it was quenched in ice-water and petr. ether. The product, after being washed, was fractionated. The isomeric forms of ionone were estd. by their ultraviolet absorption spectra. At  $-60^\circ$  the product is almost devoid of  $\beta$ -ionone even for long runs; at  $-40^\circ$  either isomer can predominate depending on the duration of the reaction (prolonged run gives 89%  $\beta$ -form, short run - 72%  $\alpha$ -form) and at this temp even 95%  $H_2SO_4$  may be used. At higher temp. the formation of  $\alpha$ -ionone rises rapidly at  $10^\circ$  almost no  $\alpha$ -ionone is formed regardless of the contact time. Decreased amount of  $H_2SO_4$  (equimolar) tends to increase the content of the  $\alpha$ -isomer in the product, but increased amount of  $H_2SO_4$  beyond 6:1 molar ratio does not produce any significant changes. Evidently  $\alpha$ -ionone is the primary cyclization product and this isomerizes to  $\beta$ -form especially rapidly at elevated temp. (almost no reaction occurs at  $-60^\circ$ ). The isomerization is repressed when only 1 mole  $H_2SO_4$  is used for mole of reactant.  $H_3PO_4$  or 60%  $H_2SO_4$  are incapable of inducing the isomerization.

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Polarography of copper *Organic*  $\alpha$ -alaninate.

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Doklady Akad. Nauk SSSR, 124, 1069-70 (1959).

Polarographic behavior on dropping Hg electrode was studied for both forms of Cu alaninate (cf. Goldbraikh, Zhur. Neorg. Khim. 1, 1739 (1956)). The study made in 0.1N  $K_2SO_4$  background electrolyte with gelatin maximum suppressor and mercurous sulfate anode, the half-wave potentials of the needle and the plate forms of the salt were found to be different; the needle form has more pos. reduction potential, the actual values being dependent on the concn. of the salt. The results are shown graphically. It is suggested that the needle form may be the cis isomer. The halfwave potentials of Cu glycine salt are more negative than those of the Cu alaninate and with the two substances having similar instability constants this indicates that the glycine salt has the lower specific adsorption. Both forms of Cu salt of glycine and the plate form of the alanine salt show a shift of the halfwave potential to the more pos. direction at relatively high concn. at 50°; at low concns. the halfwave potentials at 20° coincide with those at 50°. The needle form of Cu alaninate shows such a coincidence over the entire extent of the potential-concn. curve.

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*Organic*  
Effect of composition and the conditions of thermal treatment on the structure and the catalytic activity of  $Al_2O_3-ZrO_2$  catalysts.

A.M. Rubinshtein, V.A. Afanas'ev, V.M. Akimov, N.A. Pribytkova and K.I. Slovetskaya (N.D. Zelinskii Org. Chem. Inst., Moscow). Doklady Akad. Nauk SSSR, 124, 1076-79 (1959). Cf. Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1959, 814. The kinetic data on the behavior of  $Al_2O_3-ZrO_2$  catalysts in decompn. of iso-PrOH are shown graphically in relation to the mode of treatment and the compn. of the catalysts. These catalysts were active at 230°, while pure  $ZrO_2$  begins to function only at 300°. About 15 mole %  $ZrO_2$  is the optimum compn. of the catalyst. The catalyst components, even after heating

to 400-750° show in their X-ray diffraction patterns the distinct features of individual  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{ZrO}_2$ ; no solid solns. are formed. The best catalyst activity is found for specimens heat treated at about 600°.

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*Organic*

Oxidation of n-butane in acetic acid solution by air under pressure.

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Doklady Akad.Nauk SSSR, 124, 1083-84 (1959).

Kinetic curves are shown for the air oxidation of butane under 60 atm. at 150-165°, with yield curves being shown for  $\text{EtOAc}$ ,  $\text{MeCOEt}$  and  $\text{AcOH}$ . The latter was used as an inert solvent for the reaction which was run in steel autoclave with a Ti liner. Co stearate catalyst was used at 0.018% concn. relative to the solvent weight. The duration of runs was 6 hrs. and various rates of air flow were employed to give the kinetic data. Temps. above critical were found to be most desirable as they gave the highest yields of  $\text{AcOH}$  and the use of the catalyst is desirable for the same reason. All numerical data are in graphical form.

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*Original*

Synthesis of organomercury compounds from hydrazones. 2. Reaction of hydrazones of aldehydes and ketones of the alicyclic and the aromatic series with mercuric acetate.

A.N.Nesmeyanov, O.A.Reutov, A.S.Loseva and M.Ya.Khorlina (M.V.Lomonosov State Univ., Moscow). Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk, 1959, 50-61. Cf. this j. 1958, 1315.

To 28.5 g.  $\text{Hg}(\text{OAc})_2$  and 1 g.  $\text{Cu}(\text{OAc})_2$  in 250 ml.  $\text{H}_2\text{O}$  at  $90^\circ$  there was added dropwise 5 g. cyclohexanone hydrazone; the exothermic reaction produced  $\text{N}_2$  and  $\text{Hg}_2(\text{OAc})_2$  and finally Hg. The filtered soln. was cooled yielding 1 g. 1-acetomercuri-1-cyclohexene, m.  $116-16.5^\circ$  ( from  $\text{NaOH}$  ). The filtrate treated with  $\text{KCl}$  gave 5 g. 1-chloromercuri-1-cyclohexene, (I), m.  $191-92^\circ$  ( from  $\text{MePh}$  ). Similarly,  $\text{KBr}$  gave 1-bromomercuri-1-cyclohexene, m.  $174-75^\circ$  ( from  $\text{MePh}$  ), while  $\text{KI}$  similarly gave 1-iodomercuri-1-cyclohexene, m.  $177-78^\circ$  ( from  $\text{MePh}$  ). I ( 5 g. ) in 10 ml.  $\text{EtOH}$  was treated with 8.2 g.  $\text{NaOH}$  in 65 ml.  $\text{H}_2\text{O}$ , mixed with 3.3 g.  $\text{SnCl}_2$  in 43 ml.  $\text{H}_2\text{O}$ ; Hg pptd. immediately and an unpleasant odor developed; after being shaken 1 hr. in the cold, the mixture was extd. with  $\text{Et}_2\text{O}$  yielding 86% bis-1-cyclohexenylmercury, b<sub>10</sub>  $170^\circ$  ( some decompn. ); with dil.  $\text{HCl}$  it gave I. Heating I with concd.  $\text{HCl}$  on steam bath gave  $\text{HCl}$  and cyclohexene. If the reaction mixture of cyclohexene and  $\text{Hg}(\text{OAc})_2$  is kept 2 days in  $\text{H}_2\text{O}$ , then filtered and treated with  $\text{KCl}$ , there is formed 90% 1-chloromercuricyclohexanol, m.  $151-52^\circ$ . To 42.6 g.  $\text{Hg}(\text{OAc})_2$  suspended in 200 ml.  $\text{C}_6\text{H}_6$  there was added at  $70^\circ$  dropwise 5 g. cyclohexanone hydrazone in 50 ml.  $\text{C}_6\text{H}_6$  and the mixture was filtered after 10 min., and evapd. at room temp. yielding (II) a red oil of 1-acetoxy-1-acetoxymercuricyclohexane, which decomposed on standing and evolved Hg; alkali decomposed it rapidly to Hg and cyclohexanone; alc.  $\text{CaCl}_2$  gave 1-acetoxy-1-chloromercuricyclohexane, m.  $101-105^\circ$  ( from  $\text{Et}_2\text{O}$  ). II with cold, alc.  $\text{KOH}$  gave Hg and cyclohexanone, isolated as the dinitrophenylhydrazone. Reaction of 25.3 g.  $\text{Hg}(\text{OAc})_2$  and 5 g. 4-methylcyclohexanone hydrazone in  $\text{H}_2\text{O}$  in the presence of 1 g.  $\text{Cu}(\text{OAc})_2$  gave after the above-described treatment, using aq.  $\text{KCl}$ , 1.6 g. 4-methyl-

1-chloromercuricyclohexene, m.  $171-71.5^{\circ}$  ( from MeOH ). If  $\text{Cu}(\text{OAc})_2$  is omitted and the reaction is run in MeOH, the final treatment with KCl gave 4-methyl-1-methoxy-1,2-bis(chloromercuri)-cyclohexane, dec.  $130-40^{\circ}$  ( from  $\text{CHCl}_3$ -MeOH ), which is decomposed by KOH to Hg and by HCl to  $\text{HgCl}_2$  and 4-methylcyclohexanone. From 37.9 g.  $\text{Hg}(\text{OAc})_2$ , 250 ml.  $\text{C}_6\text{H}_6$  and 5 g. above hydrazone there was formed after filtration and evapn. 9.3 g. oily 4-methyl-1-acetoxy-1-~~chloromercuri~~mercuricyclohexane, which yields  $\text{Hg}_2(\text{OAc})_2$  with standing, while alc. KOH decomposes it to Hg and 4-methylcyclohexanone; treated with 10% KCl it gave 4-methyl-1-acetoxy-1-chloromercuricyclohexane, m.  $159-60^{\circ}$ . This with alc. KOH gave the original ketone in the cold. To 50 g. 85%  $\text{N}_2\text{H}_4$  hydrate and a little BaO there was added 50 g. cyclopentanone, stirred 2 hrs. and extd. with  $\text{Et}_2\text{O}$  yielding 87% cyclopentanone hydrazone, b<sub>5</sub>  $60-61^{\circ}$ , b<sub>21</sub>  $90-91^{\circ}$ , d<sub>20</sub> 1.0030, n<sub>D</sub><sup>20</sup> 1.5083. This ( 5 g. ) was added at  $60^{\circ}$  to 32 g.  $\text{Hg}(\text{OAc})_2$  in  $\text{H}_2\text{O}$ , as above, and after removal of the resulting Hg, the cooled filtrate was treated with KCl yielding 3 g. 1,1'-bis-~~syn~~chloromercuridicyclopentyl ether, dec. above  $120^{\circ}$  ( from aq.  $\text{Na}_2\text{CO}_3$  ), which decomposes rapidly in light and moisture. With alc. KOH this gave Hg and cyclopentanone, isolated as the dinitrophenylhydrazone. If the above prepn. is run in MeOH, the product is 1-methoxy-1-chloromercuricyclopentane, a colorless solid, which decomposes in air and light. Reaction of camphor hydrazone with  $\text{Hg}(\text{OAc})_2$  as above in  $\text{C}_6\text{H}_6$  gave an oily 1,1'-di(acetoxymercuri)dibornyl ether, which is decomposed by alc. KOH or HCl; the oil decomposes at  $100^{\circ}$  yielding Hg; treated with alc.  $\text{CaCl}_2$  it gave 1,1'-di(chloromercuri)dibornyl ether, (III) m.  $153-55^{\circ}$  ( from  $\text{Et}_2\text{O}$  ), which with concd. KOH gave camphor, while heating with concd. HCl gave bornyl chloride. III was also formed in 98% yield from  $\text{Hg}(\text{OAc})_2$  and camphor hydrazone in  $\text{CCl}_4$ , after treatment with  $\text{CaCl}_2$  as above. Use of excess  $\text{Hg}(\text{OAc})_2$  in the reaction with camphor hydrazone in  $\text{H}_2\text{O}$ , and treatment with 10% KCl, gave  $\alpha,\beta,\beta,\beta$ -tetrakis-(chloromercuri)dibornyl ether, dec.  $210^{\circ}$  ( from aq.  $\text{Na}_2\text{CO}_3$  ).